

In Situ Chemical Oxidation

Arun Gavaskar

Battelle Memorial Institute

and

Charles Reeter

Naval Facilities Engineering Service Center

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

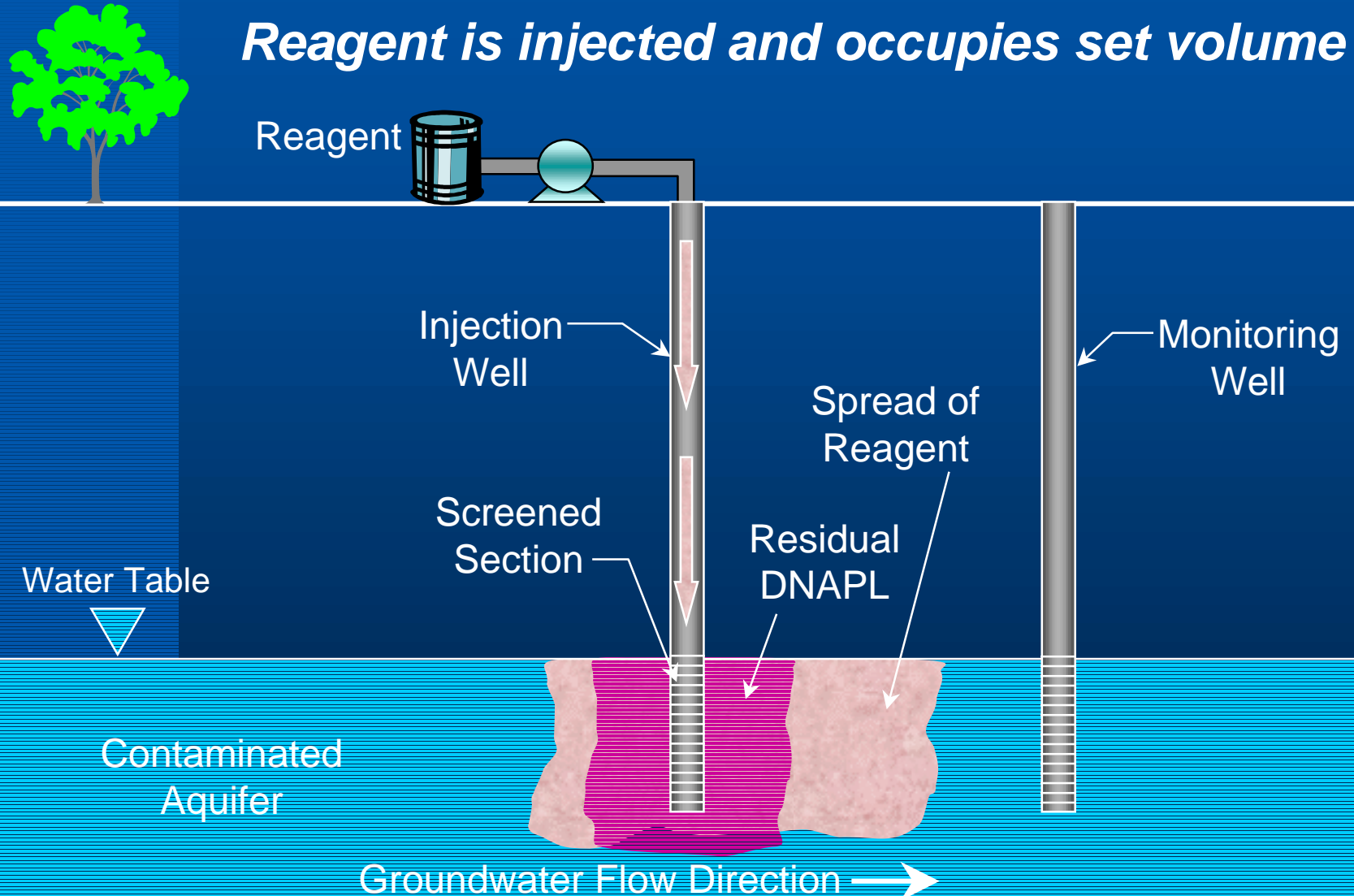
Definitions

- In situ chemical oxidation is the application of a strongly oxidizing agent in the ground via well injection or a specially designed injection tool.
- Migration of the oxidant can be controlled hydraulically using arrays of injection and/or extraction wells.
- Oxidants degrade contaminants by converting them to benign compounds, ideally H_2O , CO_2 , and mineral salts. However, intermediate byproducts also may be formed.
- Contaminants amenable to in situ chemical oxidation treatment include PCE, TCE, some aromatic compounds (PAHs), amines, and nitro compounds.

In Situ Chemical Oxidation

Oxidant Injection Process

Reagent is injected and occupies set volume



In Situ Chemical Oxidation

Definitions

- Can be used to treat dense, nonaqueous-phase liquid (DNAPLs) as well as dissolved-phase contaminants
- Does not rely on biological processes
- May not require aboveground treatment, as with pump and treat (P&T) systems, thermal heating, and surfactant flushing
- Accelerates or replaces P&T systems

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

Background Information

Oxidation: The result of atoms or molecules losing electrons, due to reactions with other species

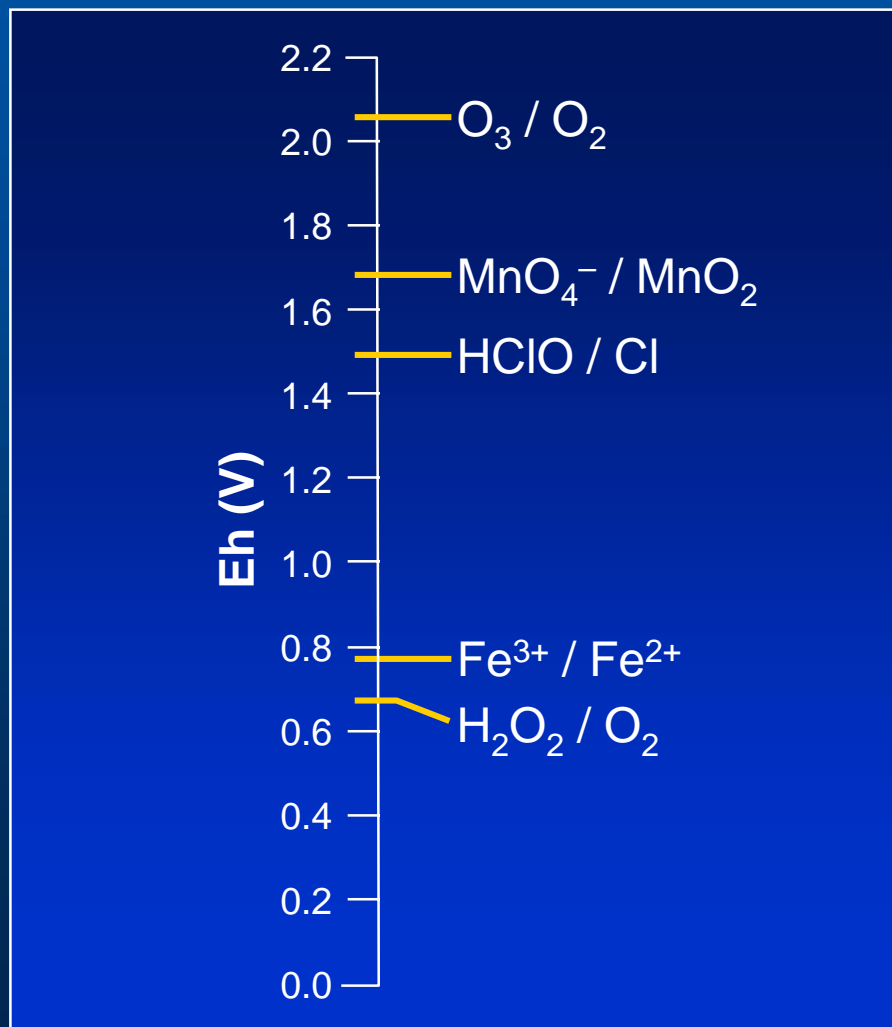
ORP: Oxidation-reduction potential (measured in the field or laboratory)

Eh: Redox potential (calculated relative to the Standard Hydrogen Electrode)

Free Radicals: Species with unpaired electrons, which are highly reactive with other species and with one another (e.g., OH^\bullet or H^\bullet)

In Situ Chemical Oxidation

Standard Reduction Potentials for Selected Redox Couples



In Situ Chemical Oxidation

Example of a Redox Reaction

- Oxidation

- Increase in oxidation number (loss of electrons)

- Reduction

- Decrease in oxidation number (gain of electrons)



- Oxidation number of hydrogen has increased from 0 to +1

- Hydrogen has been oxidized

- Oxygen is the oxidizing agent
- Oxygen has been reduced

In Situ Chemical Oxidation

Typically Used Chemical Oxidants

- Fenton's Reagent (liquid): $\text{Fe}^{2+} + \text{H}_2\text{O}_2$
- Potassium Permanganate (liquid): KMnO_4
- Ozone (gas): O_3

In Situ Chemical Oxidation

Chemistry of Fenton's Reagent

Chain initiation creates free radicals



Free radicals contribute to oxidation of contaminants



Oxidation of organic radicals regenerates ferrous iron and propagates reaction



In Situ Chemical Oxidation

Field Implementation of Fenton's Reagent

- Reagent is widely used in wastewater treatment
- Key factor is generation of hydroxyl radicals, which are powerful, non-specific oxidizing agents
- Ferrous iron (Fe^{2+}) acts to catalyze the oxidation reaction, which subsequently produces ferric iron (Fe^{3+})
- Optimum pH range is 5 to 6
- Ferric iron is regenerated back to ferrous iron by reaction with organic radicals or additional H_2O_2
- Reaction rate is rapid

In Situ Chemical Oxidation

Field Implementation of Fenton's Reagent



Monitoring H_2O_2 at
DoD Housing Facility Site
at Novato, CA



Injection of Fenton's Reagent
in a Well

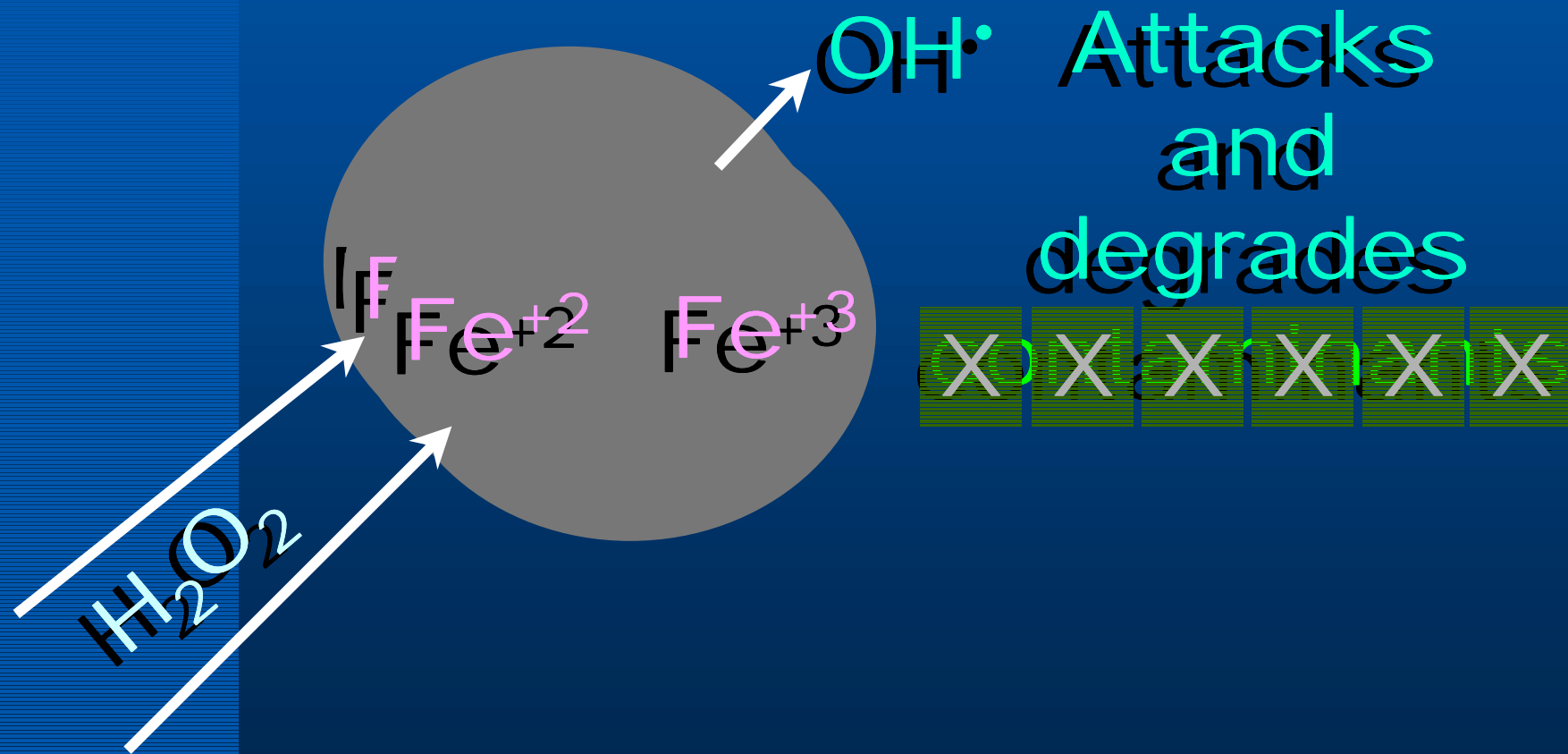
In Situ Chemical Oxidation

Field Implementation of Fenton's Reagent

- Ferrous iron (Fe^{2+} , usually as FeSO_4) can be injected along with H_2O_2 . Alternately, the process itself can reduce native ferric iron (Fe^{3+}) to supply Fe^{2+} .
- Typical concentration of injected H_2O_2 is ~10% by weight, but dilution effect in subsurface can be substantial.
- As H_2O_2 is consumed, iron remains in the ferric state (Fe^{3+}), which will readily precipitate at neutral pH as ferric hydroxide.

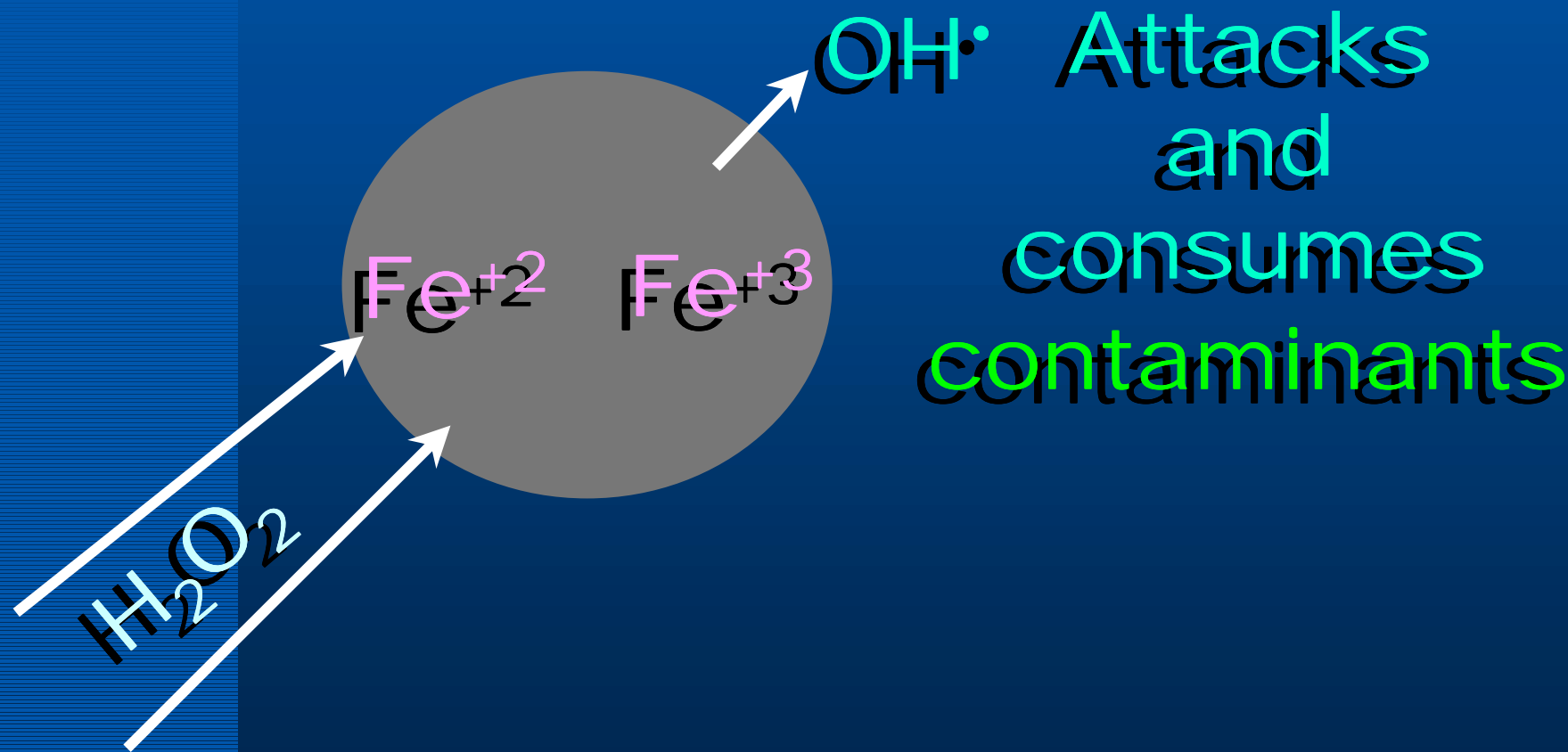
In Situ Chemical Oxidation

Fenton's Reagent Chemistry



In Situ Chemical Oxidation

Fenton's Reagent Chemistry



In Situ Chemical Oxidation

Advantages of Fenton's Reagent

- Strong oxidizing properties, fast action
- Good solubility of components (H_2O_2 and FeSO_4) in water facilitates in situ application
- Relatively inexpensive chemicals
- Relatively benign byproducts
- Reaction kinetics are solubility driven

In Situ Chemical Oxidation

Disadvantages of Fenton's Reagent

- Action is highly pH-dependent
- H_2O_2 can be explosive and highly reactive (difficult to handle)
- Reagent has a relatively short life in the aquifer
- Reagent covers relatively short distances around injection point
- FeSO_4 and H_2O_2 must be mixed immediately before injection
- Oxidation demand of native organic matter in aquifer must be satisfied

In Situ Chemical Oxidation

Typically Used Chemical Oxidants

- Fenton's Reagent (liquid): $\text{Fe}^{2+} + \text{H}_2\text{O}_2$
- Potassium Permanganate (liquid): KMnO_4
- Ozone (gas): O_3

In Situ Chemical Oxidation

Chemistry of Potassium Permanganate

Potassium permanganate dissociates in aqueous solution:



Permanganate ions oxidize PCE:



Permanganate ions oxidize TCE: :



In Situ Chemical Oxidation

Chemistry of Potassium Permanganate

- Oxidation of PCE and TCE produces:
 - CO_2 and Cl_2 gases
 - Hydrochloric and hypochlorous acids
 - Chloride and hypochlorite salts
- Side reactions:
 - CO_2 will react with water to lower the pH
 - Excess CO_2 may block pore space and further inhibit injection of permanganate
 - Precipitation of manganese dioxide (MnO_2) will remain in the aquifer as soil coatings, which could reduce permeability



KMnO_4 Holding Tank
at Cape Canaveral
Air Station, FL

In Situ Chemical Oxidation

Field Implementation of Potassium Permanganate

Example field setup of in situ KMnO_4 application



In Situ Chemical Oxidation

Field Implementation of Potassium Permanganate

Potassium permanganate is a more selective oxidizing agent than Fenton's Reagent. For example, permanganate preferentially attacks double bonds, but has little effect on single bonds. Therefore, **chlorinated ethenes** like **DCE, TCE, and PCE** are **good candidates** for treatment.

Potassium permanganate **would not** be a preferred chemical oxidant for treating **chlorinated ethanes**, such as **methylene chloride, carbon tetrachloride, 1,1-DCA, and 1,1,1-TCA**.

In Situ Chemical Oxidation

Method-Specific Considerations of Potassium Permanganate

- Loss of porosity possible due to buildup of MnO_2 (precipitate)
- May need to control concentration of soluble Mn^{2+} to prevent long-range transport within the aquifer
- Applicable over a wider pH range than Fenton's Reagent

In Situ Chemical Oxidation

Advantages of Potassium Permanganate

- KMnO_4 is:
 - Easy to handle
 - Much more stable in the environment than Fenton's Reagent
 - Relatively inexpensive
- High solubility in water facilitates in situ application
- Strong oxidizing capabilities, fast action
- Action is relatively pH-independent

In Situ Chemical Oxidation

Disadvantages of Potassium Permanganate

- Oxidation demand of native organic matter in aquifer must be satisfied
- Reaction kinetics are solubility driven
- Byproducts (e.g., MnO_2 , Mn^{2+} , and KCl) may require special handling
- Industrial-grade KMnO_4 typically contains trace metals that may be a regulatory concern

In Situ Chemical Oxidation

Typically Used Chemical Oxidants

- Fenton's Reagent (liquid): $\text{Fe}^{2+} + \text{H}_2\text{O}_2$
- Potassium Permanganate (liquid): KMnO_4
- Ozone (gas): O_3

In Situ Chemical Oxidation

Chemistry of Ozone in Water



- Rate of O_3 degradation depends on pH

In Situ Chemical Oxidation

Field Implementation of Ozone Treatment

- Ozone is a gas that is a strong oxidizing agent
- Ozone is 12 times more soluble than O_2 in water (i.e., ~100 mg/L vs. 8 mg/L), but less soluble than $KMnO_4$ or Fenton's Reagent
- The usual limitations of gas sparging (e.g., channeling) apply to ozone injection
- Ozone is relatively expensive to generate and cannot remain stable in an aquifer for long periods
- Reactivity of ozone may make handling difficult

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

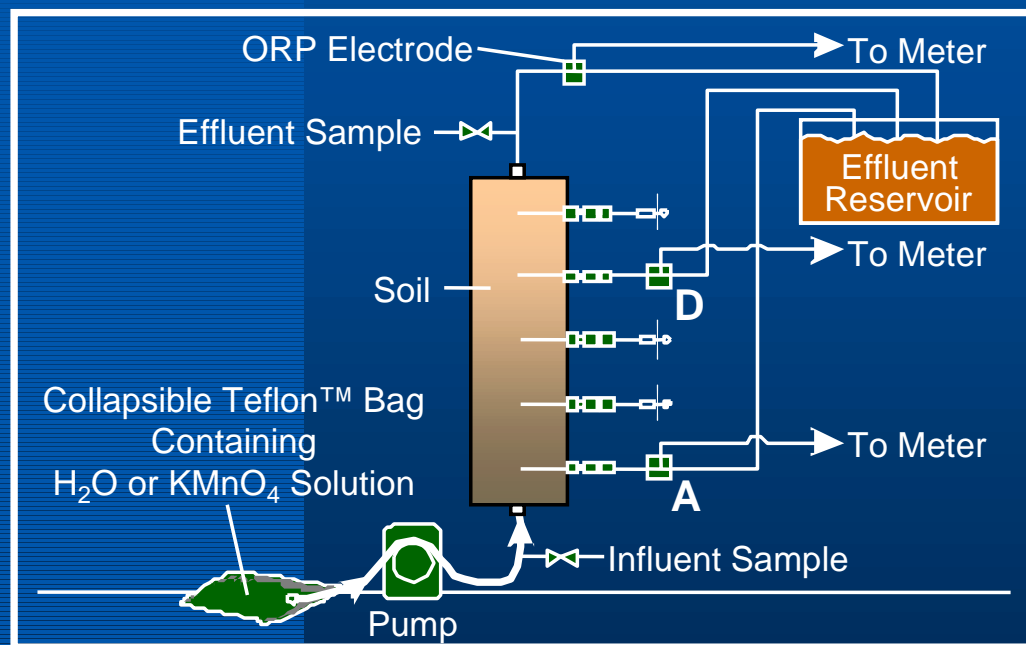
In Situ Chemical Oxidation

Important Steps in Field Implementation

- Perform adequate site characterization
 - Determine contaminant distribution
 - Calculate hydraulic properties of aquifer
 - Analyze aquifer geochemistry and organic content
- Execute treatability tests
 - Conduct batch or column tests
 - With site-specific soils
 - With industrial-grade chemicals
- Involve regulatory agencies in the design process
- Design delivery system
- Implement monitoring

In Situ Chemical Oxidation

Bench-Scale Column Test



Column Used to Simulate In Situ
Chemical Oxidation of a DNAPL
Source Zone of TCE



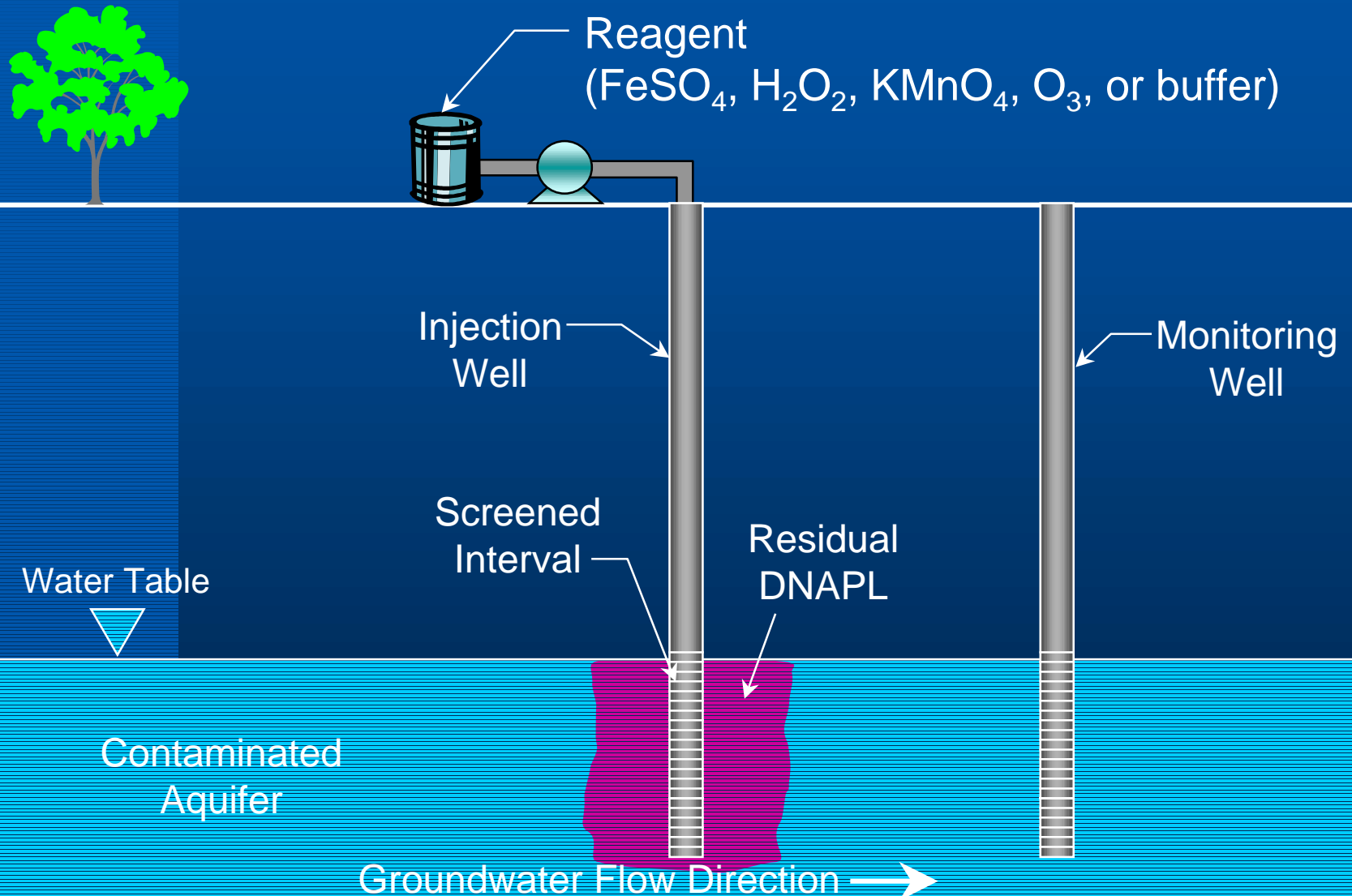
In Situ Chemical Oxidation

Field Implementation Considerations

- Chemical oxidants are good options for many recalcitrant compounds
- Chemical oxidation can be applied at greater depths than possible by treatment methods that rely on excavation equipment
- Technology works best in homogeneous soils
- Technology helps meet rapid schedule requirements

In Situ Chemical Oxidation

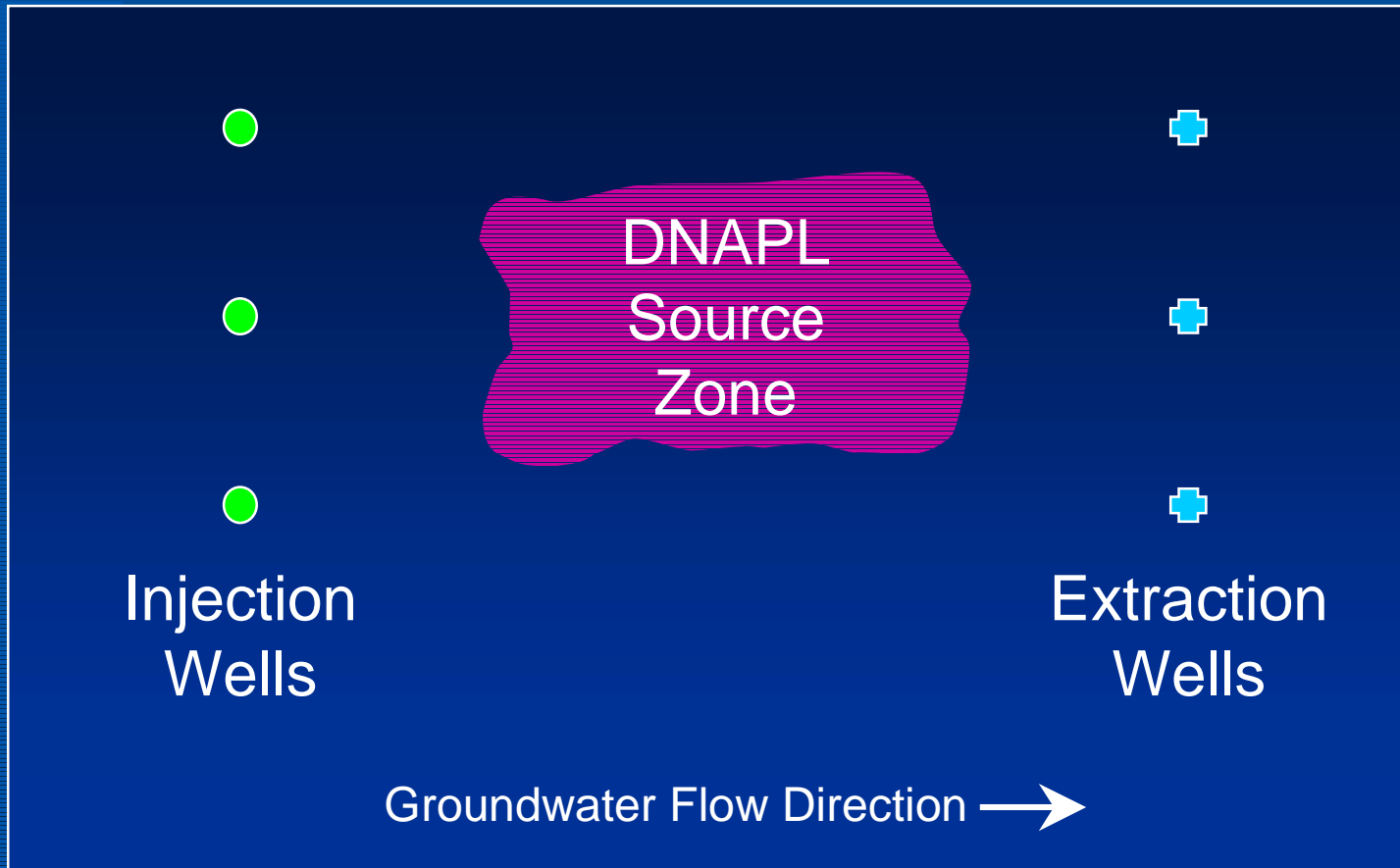
Field Implementation: Injection



In Situ Chemical Oxidation

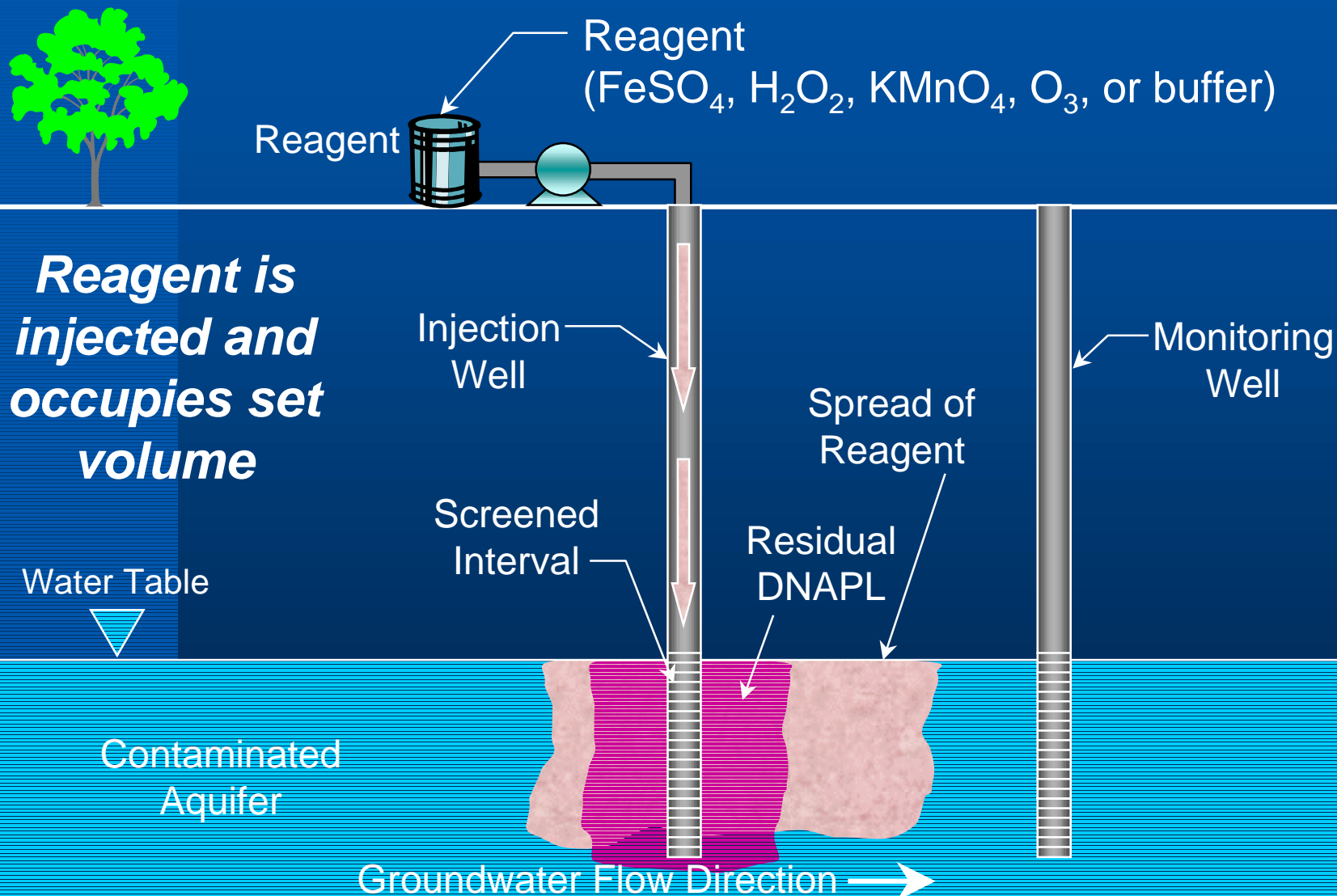
Field Implementation: Injection and Extraction

Plan View



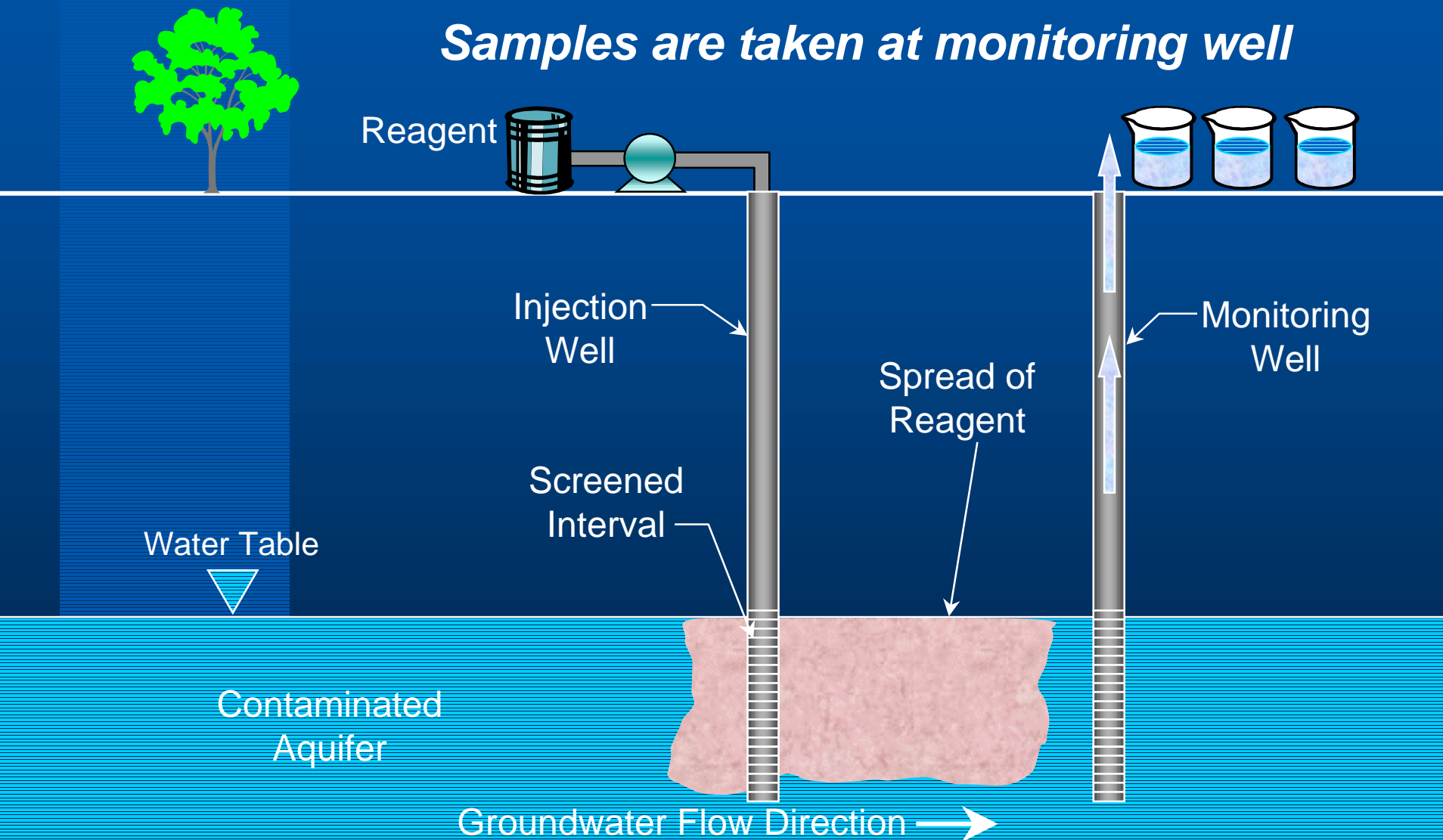
In Situ Chemical Oxidation

Field Implementation: Oxidant Injection Process



In Situ Chemical Oxidation

Field Implementation: Monitoring Process (ideal conditions)



In Situ Chemical Oxidation

Evaluation of a Potential Site for Treatment

- Contaminants must be amenable to oxidation
- Impact of groundwater chemistry (alkalinity, phosphate, citric/oxalic acid, EDTA) must be determined
- Aquifer preferably has low level of native organic matter
- Hydraulic properties of aquifer must be determined
- Heterogeneities in soil formation that can disproportionately conduct or obstruct in situ reagent flow must be identified
- May require hydraulic control to prevent spread of contaminants due to injection pressures

In Situ Chemical Oxidation

Mass Transfer Considerations

- Immiscibility of oxidant solutions (Fenton's Reagent or KMnO_4) with (DNAPLs) means that reactions take place in the aqueous phase. Therefore, rate of reaction is limited by interphase mass transfer.
- The mass transfer rate can be improved by increasing the oxidant concentration, which in turn increases the concentration gradient across the interface. Surfactants or alcohols also may be added to KMnO_4 to help solubilize the contaminant.

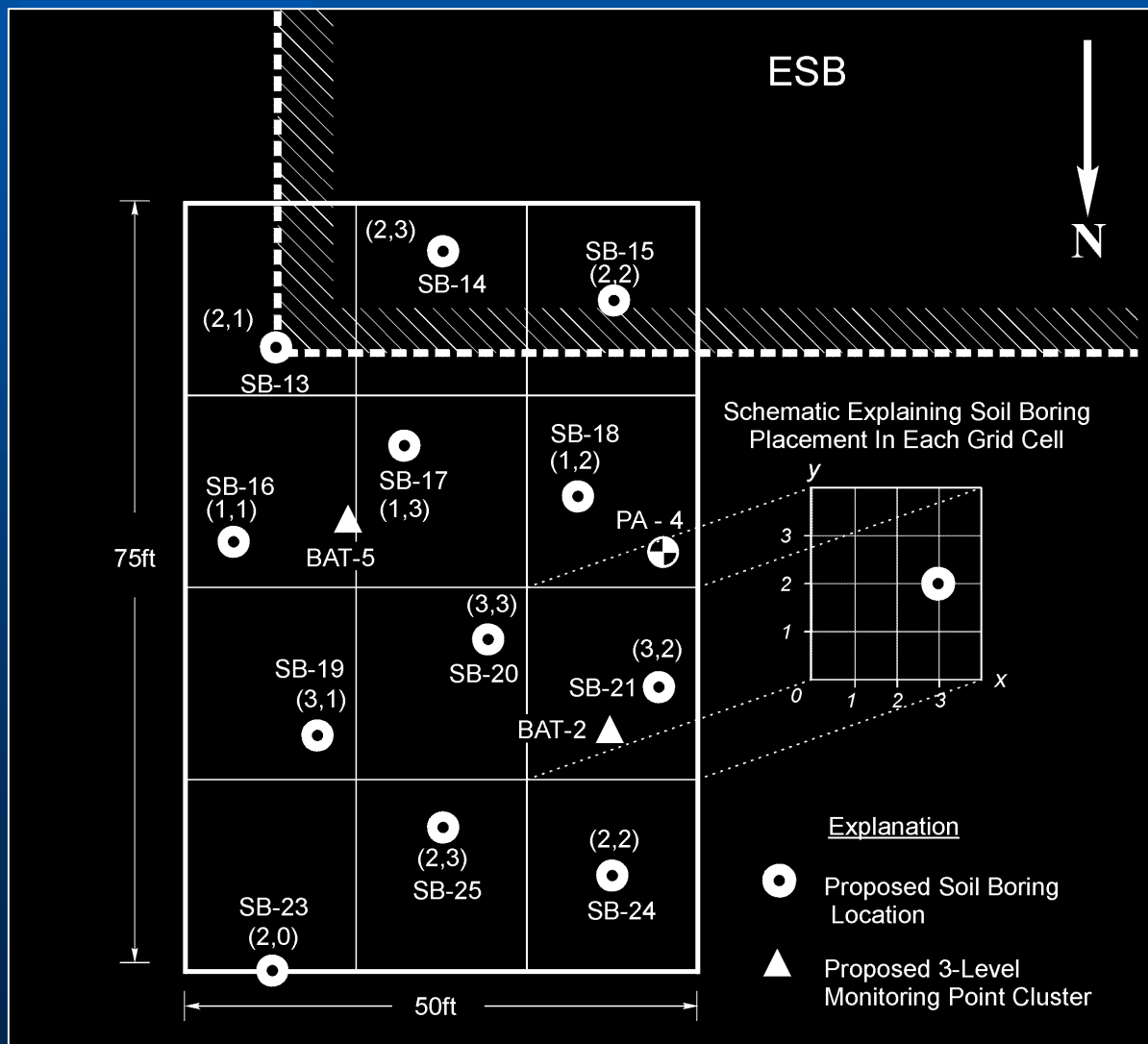
In Situ Chemical Oxidation

Pilot Test: LC34 Site, Cape Canaveral Air Station, FL



In Situ Chemical Oxidation

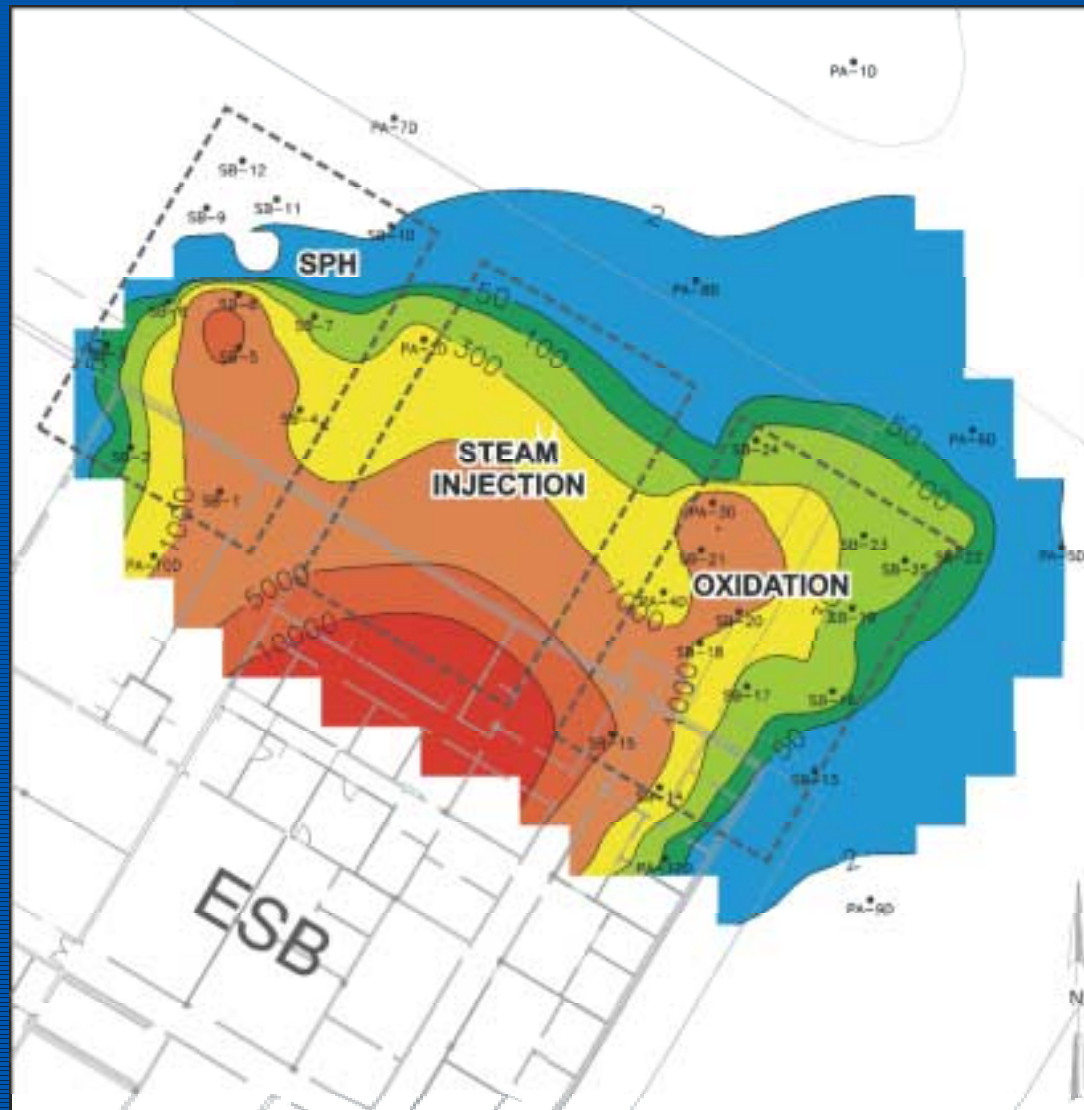
Pilot Test: LC34 Site, Cape Canaveral Air Station, FL



Statistical Design of
Soil Boring Locations
in One of the Test Plots
at LC34

In Situ Chemical Oxidation

Pilot Test: LC34 Site, Cape Canaveral Air Station, FL

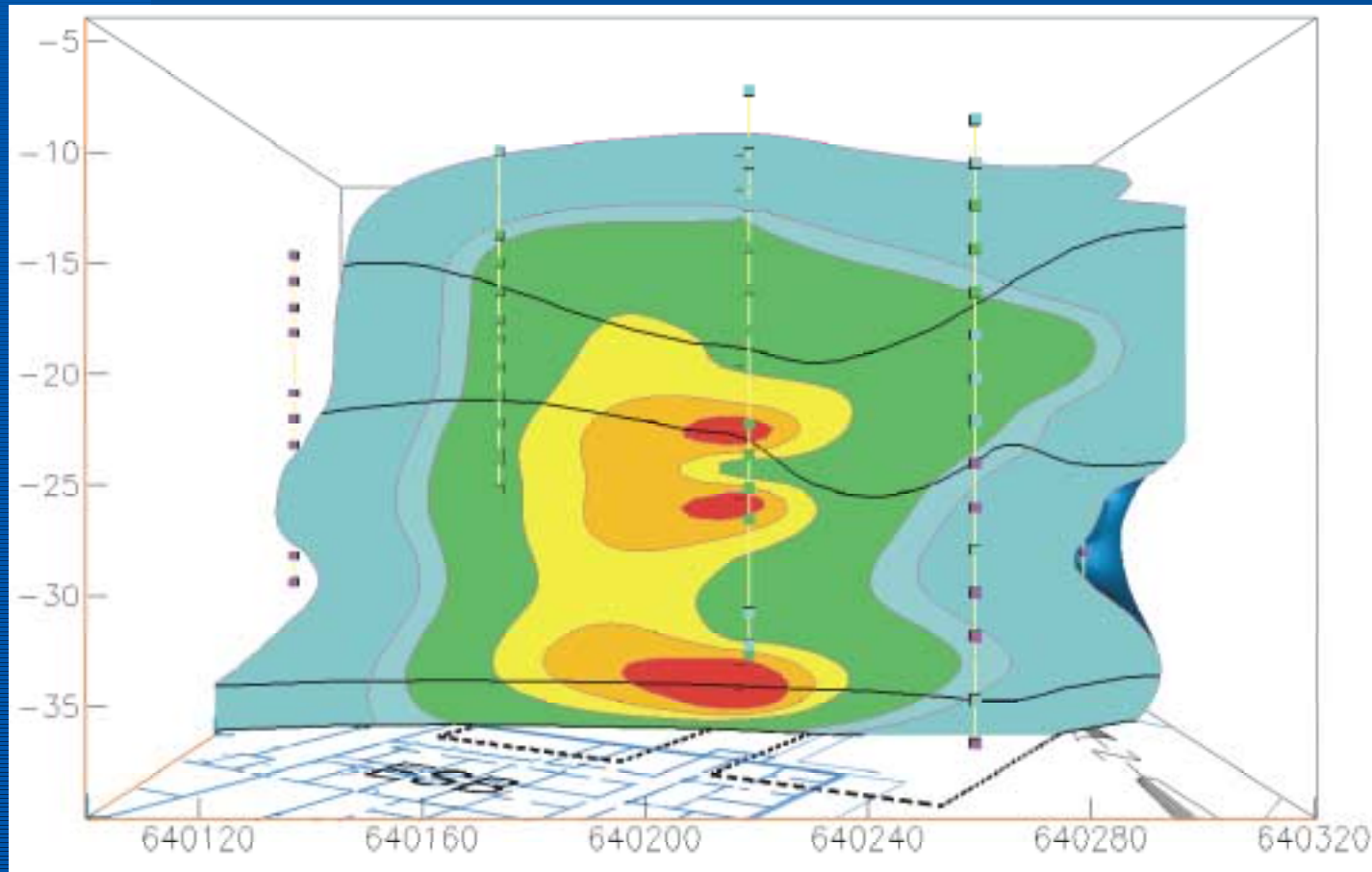


TCE Soil
Concentrations
(µg/kg) at LC34

In Situ Chemical Oxidation

Pilot Test: LC34 Site, Cape Canaveral Air Station, FL

3-D Image of TCE Distribution
in Soil Within the Subsurface at LC34



Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

Cost Factors that Drive Economics

- Cost of reagents
 - O_3 more expensive than $KMnO_4$ or Fenton's Reagent
- Dosage
 - Depends on native organic matter levels and contaminant concentrations
- Oxidation kinetics
 - Solubility-driven
 - Geochemistry
- Target cleanup levels
- Nature of (and control over) byproducts
- Level of monitoring required
- Hydraulic controls required to mitigate potential for contaminant migration

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

Regulatory Concerns

- Spread of contaminants due to injection pressures
 - Application of oxidant requires hydraulic control (Example: Using an array of pumping wells at the site perimeter to arrest the possible migration of the plume).
- Transport of Mn^{2+} in aquifer
 - Mn has a secondary MCL of 50 mg/L
 - If aquifer is reducing and has very low alkalinity, Mn^{2+} can be highly mobile. It may be necessary to control the migration of Mn^{2+} by chemical means (oxidation or precipitation).

In Situ Chemical Oxidation

Potential Regulatory Concerns: Monitoring Requirements

- Hydraulic gradients (water levels)
- Target contaminants
- Oxidation byproducts
 - Fe, Mn, Cl, and total dissolved solids
- Minor components of industrial-grade oxidant
 - Trace metals in permanganate
- Temperature, pH, ORP, and color

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

Summary and Conclusions

- In situ chemical oxidation can be a superior technical option for remediating recalcitrant organics in groundwater
- Application of technology is not limited by depth (but cost is an important consideration)
- Can choose between chemically selective and non-selective treatment methods
- Residual oxidizing agents are environmentally benign
- Demand for automated system components is increasing

Overview

- Definitions
- Principle
- Field Implementation
- Cost Factors
- Regulatory Concerns
- Summary
- Case Histories

In Situ Chemical Oxidation

Project Sites

<u>Site Location</u>	<u>Technology</u>	<u>Contaminant</u>
Anniston Army Depot (AL)	H ₂ O ₂	TCE
Army CRREL (NH)	KMnO ₄	TCE
NAS Pensacola (FL)	H ₂ O ₂	TCE
Nellis AFB (NV)	Ozone	TCE
Shaw AFB (SC)	H ₂ O ₂	TCA
NSB Kings Bay (GA)	H ₂ O ₂	PCE
Letterkenny Army Depot (PA)	H ₂ O ₂	PCE, TCE
DOE Savannah River Plant (SC)	H ₂ O ₂	PCE, TCE
DOE Portsmouth Plant (OH)	KMnO ₄	TCE
DOE Kansas City Plant (MO)	KMnO ₄	PCE, TCE
MCAS Cherry Point (NC)	H ₂ O ₂	BTEX

Case History: NSB Kings Bay, GA

Fenton's Reagent Project

**In Situ Chemical Oxidation and Natural Attenuation
for an Accelerated, Cost-Efficient Cleanup**



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Site Location – Sanitary Landfill

- 25-acre landfill
- 1974–1981
- Domestic waste
- Residential area west of landfill



- Flat, grassy meadow
- Fine sands with silt beds
- PCE/TCE/DCE/VC plume

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Adjacent Residential Area

- 630 Homes



- Groundwater not used for drinking water, but used for lawn irrigation, washing cars, etc.

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Chlorinated Solvents Migration

- Landfill source area:
9,000 ppb of PCE
- Roadway right-of-way:
1–170 ppb of DCE and
VC
- Subdivision area:
2–3 ppb of DCE



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Interim Measures

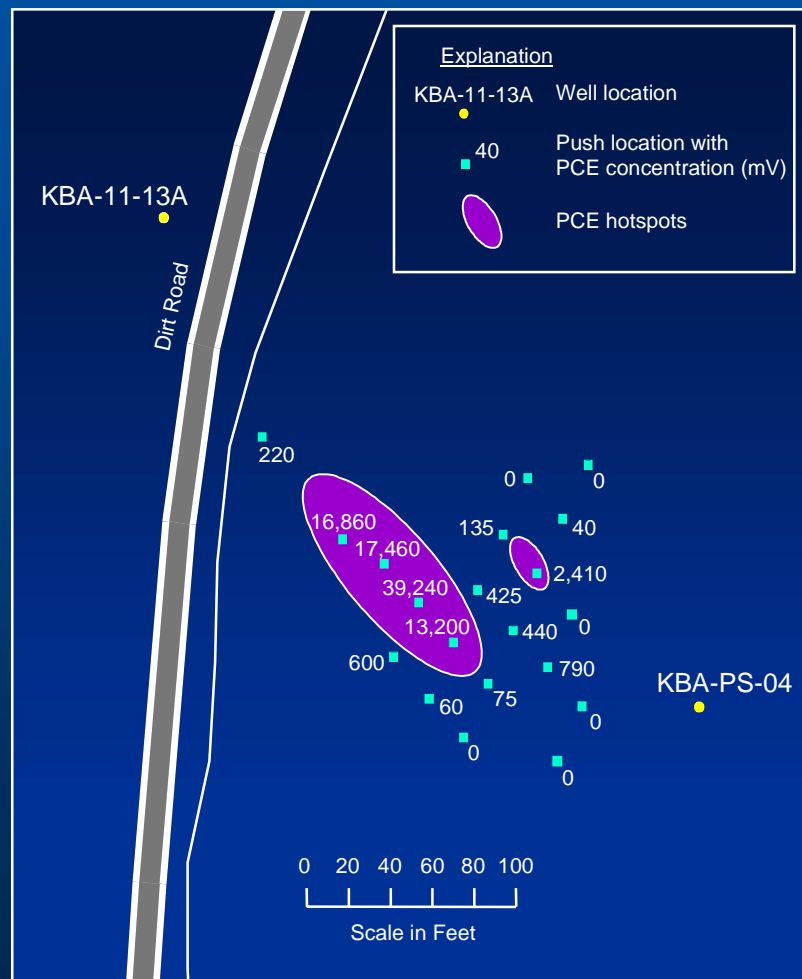
- Pump and treat (P&T) for containment implemented only at three wells between landfill and subdivision
- State requests additional wells, discusses capping
- Navy reviews source reduction techniques and natural attenuation
 - In-well stripping
 - Chemical oxidation
 - Groundwater extraction



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Site Conditions

- Landfill
 - Sulfate reducing
 - Effective reductive dechlorination of PCE and TCE
- Downgradient
 - Iron reducing
 - Microbial oxidation of DCE and VC
- Efficient natural attenuating system
- Lacks distance to degrade contaminants



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Source Reduction Goals

- Reduce to 100 ppb of total volatile organic compounds (VOCs) in source area
- Ensure that plume has degraded prior to compliance point (property line)
- Groundwater modeling suggests that the plume will collapse in 5 years

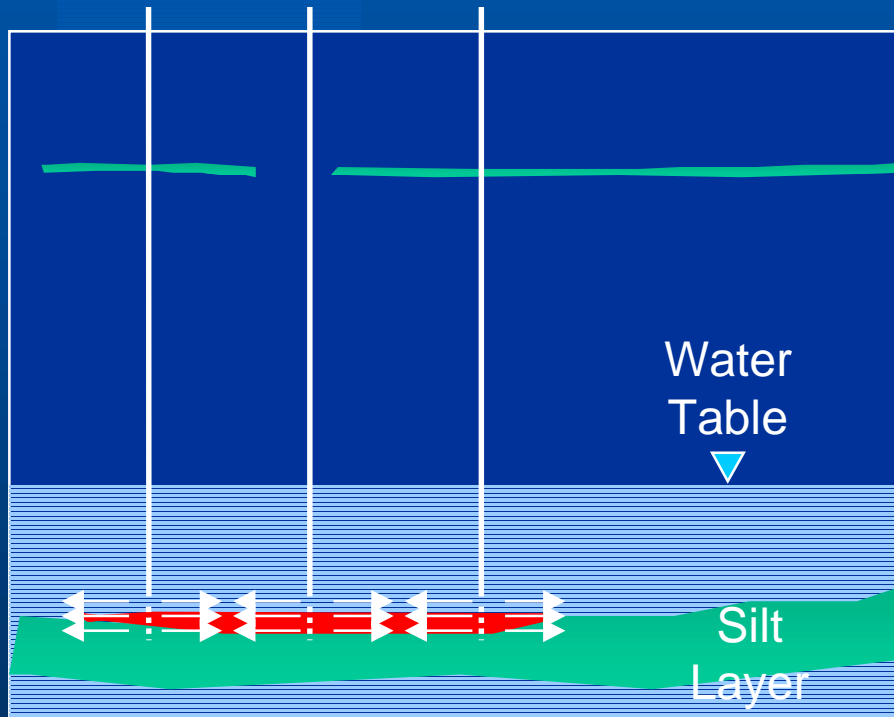
Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Cleanup Strategy

- Aggressive source reduction using chemical oxidation (Fenton's Reagent) over a 2–3 month period
- Continue pump and treat within intermediate plume area for one year
- Turn off P&T system, and monitor for natural attenuation

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Injection Wells



- Targeted into thin DNAPL accumulation zone
- Used a robust pattern of overlapping injection
- H_2O_2 and Fe^{++} were added to “burn” the DNAPL source

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Injection Process



■ Geo-Cleanse
International, Inc.

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Injection Process



- Boiling of formation water
- Ferric iron produced



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Phase I Injection Details

- Injection area 50 ft x 150 ft
- 23 injection points
- 6 monitoring wells (PVC)
- Injection wells
 - Schedule 80 (steel)
 - Injected intervals (two)
 - Shallow (29–32 ft bgs)
 - Deep (38–42 ft bgs)
- 8,250 gallons of H_2O_2 (50% solution)
- Similar amount of ferrous sulfate and buffers

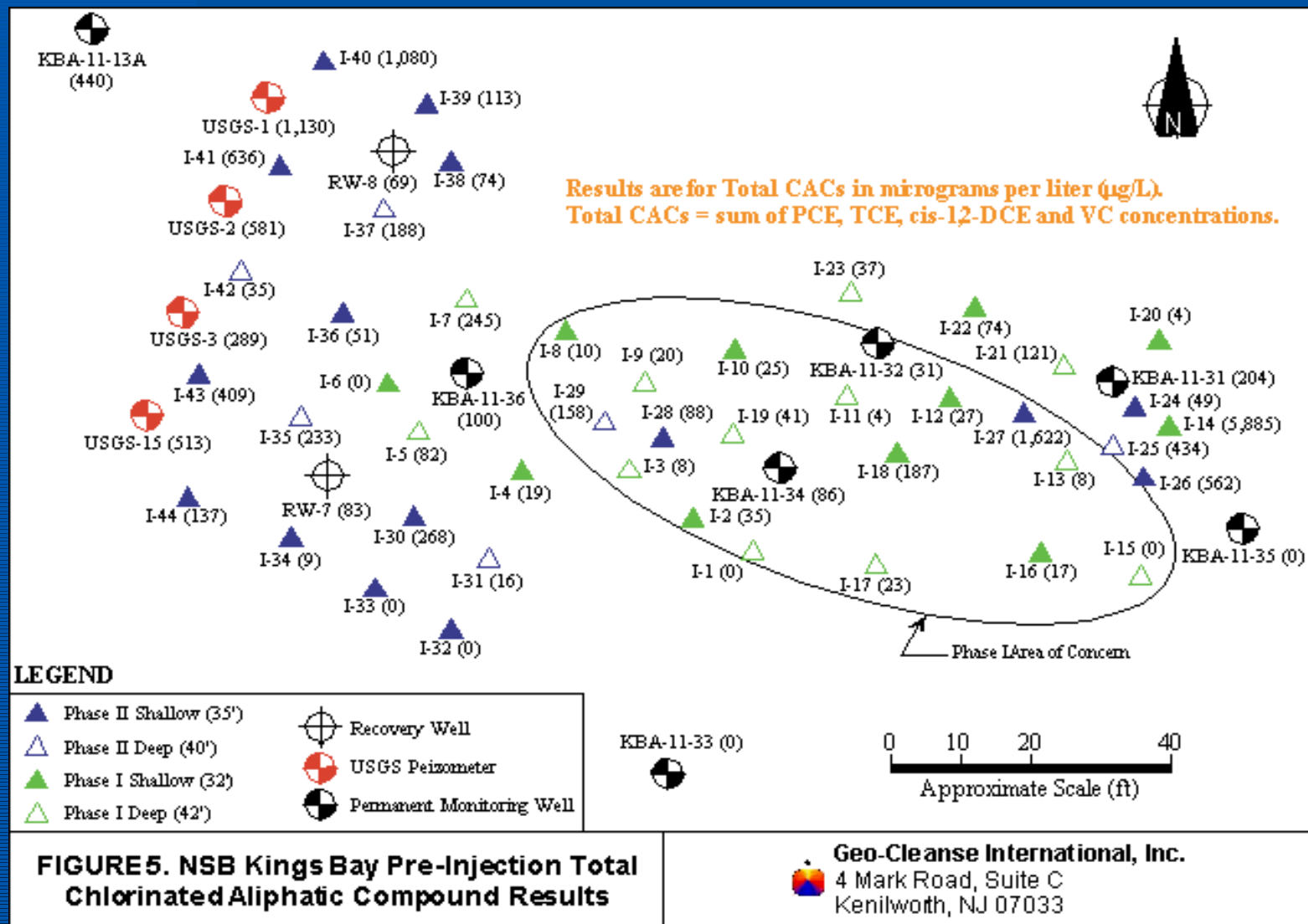
Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Phase II Injection Details

- Followup treatment for northwest area of contaminant plume (February 9–13, 1999)
- 20 injection points
- Injected intervals (two)
 - Shallow (29–32 ft bgs)
 - Deep (38–42 ft bgs)
- 3,700 gallons of H_2O_2 (50% solution)
- Similar amount of ferrous sulfate and buffers

Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Source Area and Injection Points



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: First Injection Results

Total VOCs (ppb)

Well	Pre-injection	Post-injection
KBA-11-34	9,074	93
KBA-11-32	133	25
KBA-11-36	512	416
INJ-11	200	3

Case History: NSB Kings Bay, GA

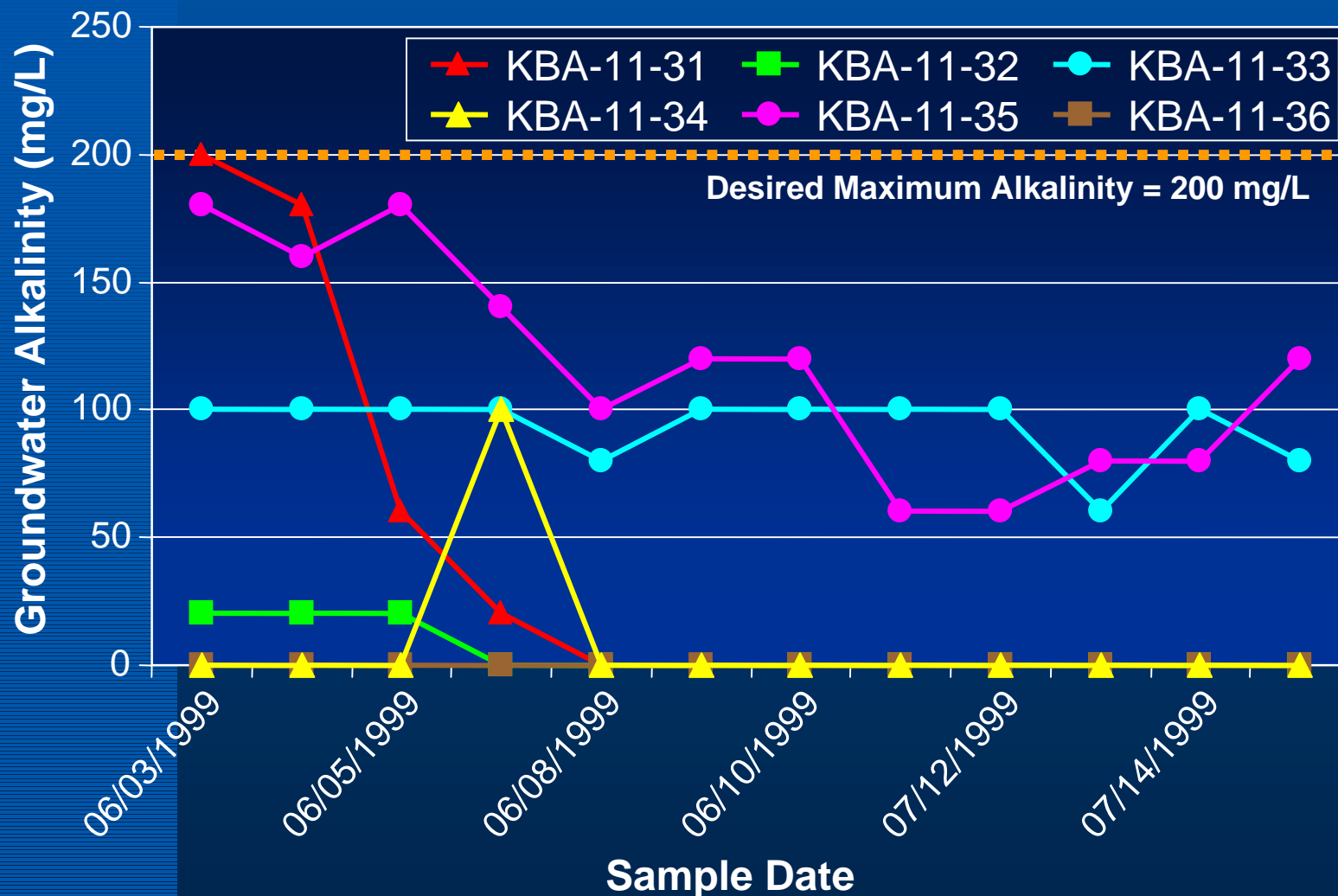
Fenton's Reagent Project: Second Injection Results

Total VOCs (ppb)

Well	No Treatment	After First Treatment	After Second Treatment
KBA-11-34	9,074	93	9
KBA-11-32	133	25	17
KBA-11-36	512	416	6
INJ-11	200	3	NS

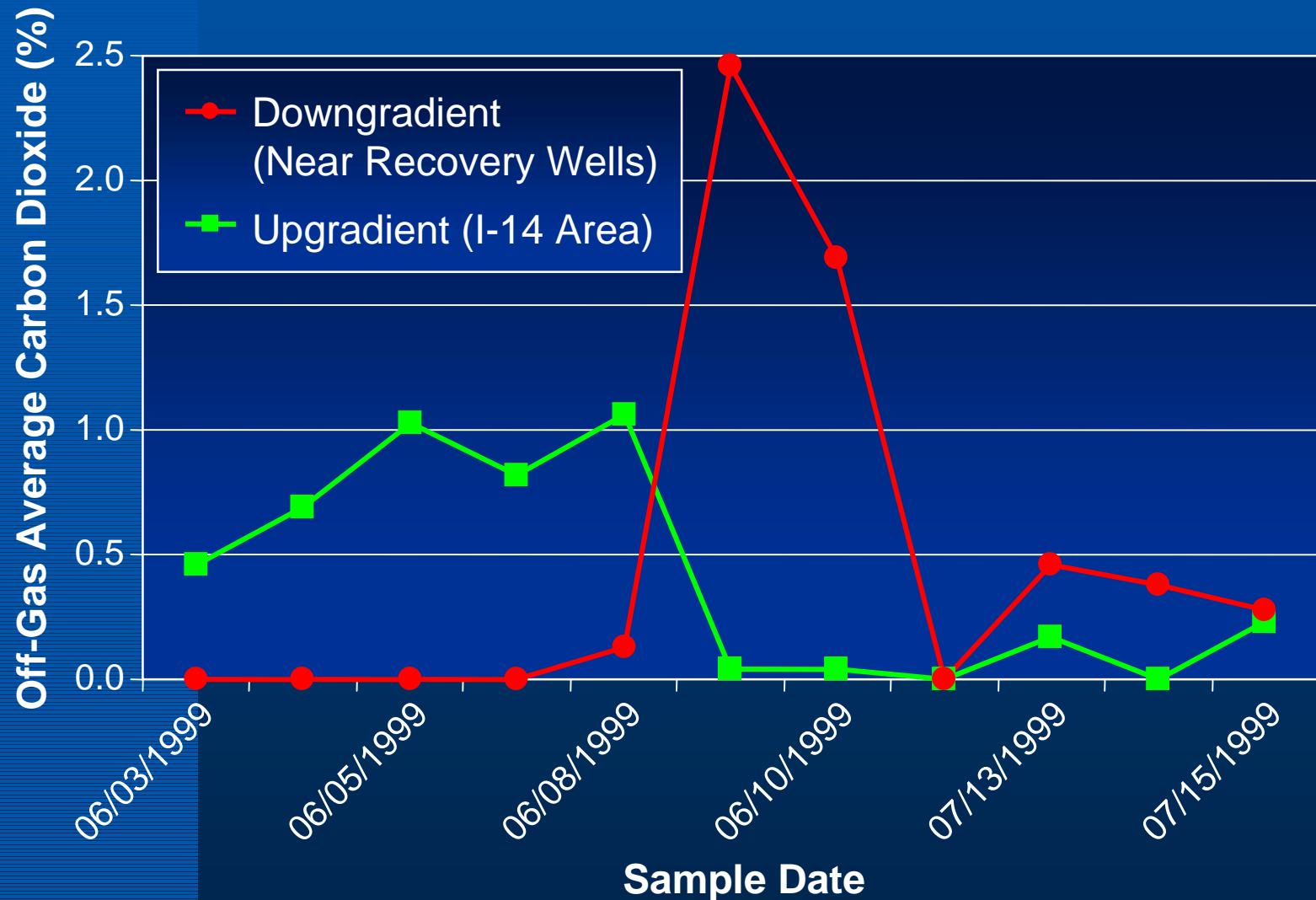
Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Groundwater Alkalinity Data



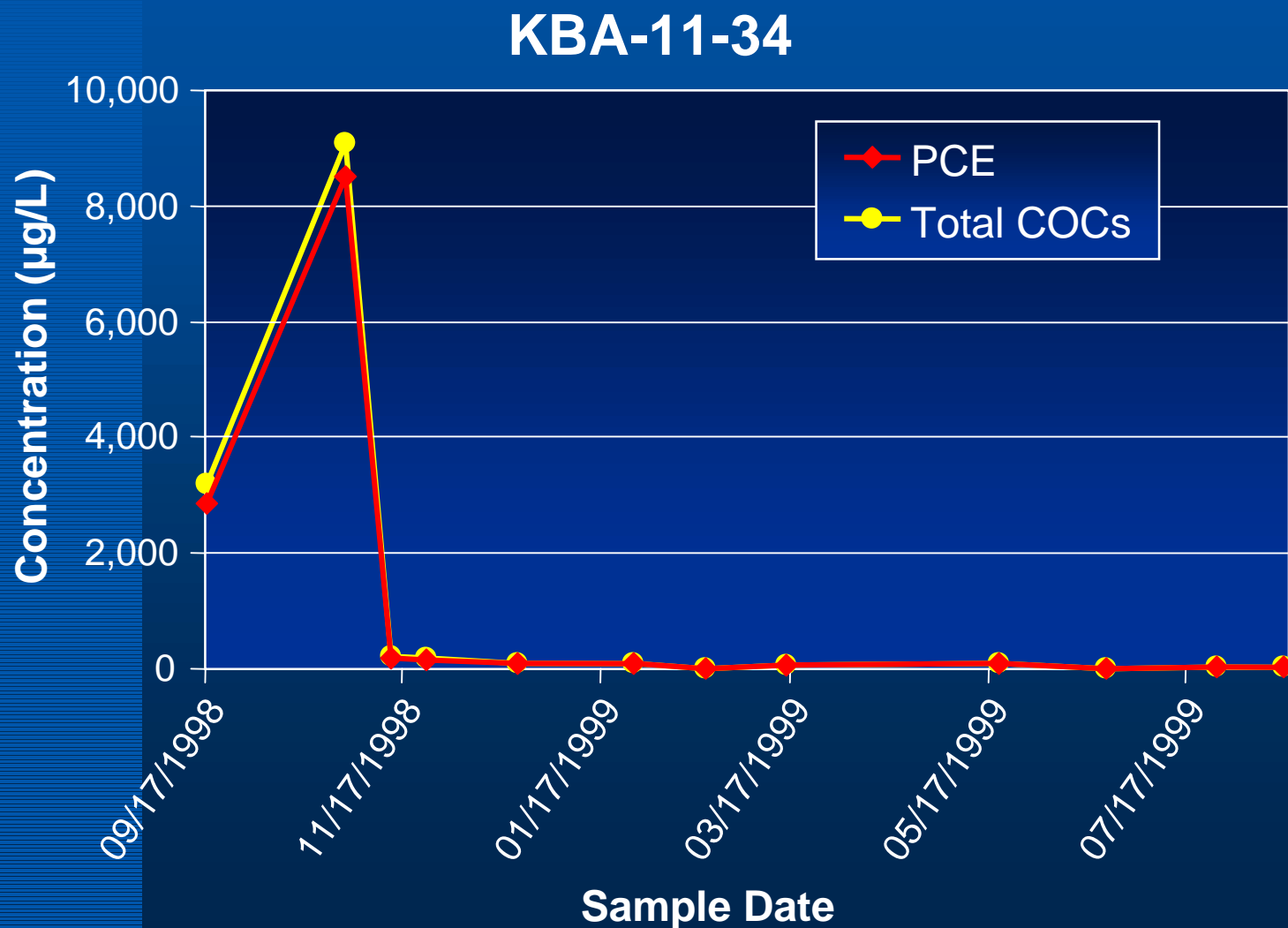
Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Off-Gas Carbon Dioxide Data



Case History: NSB Kings Bay, GA

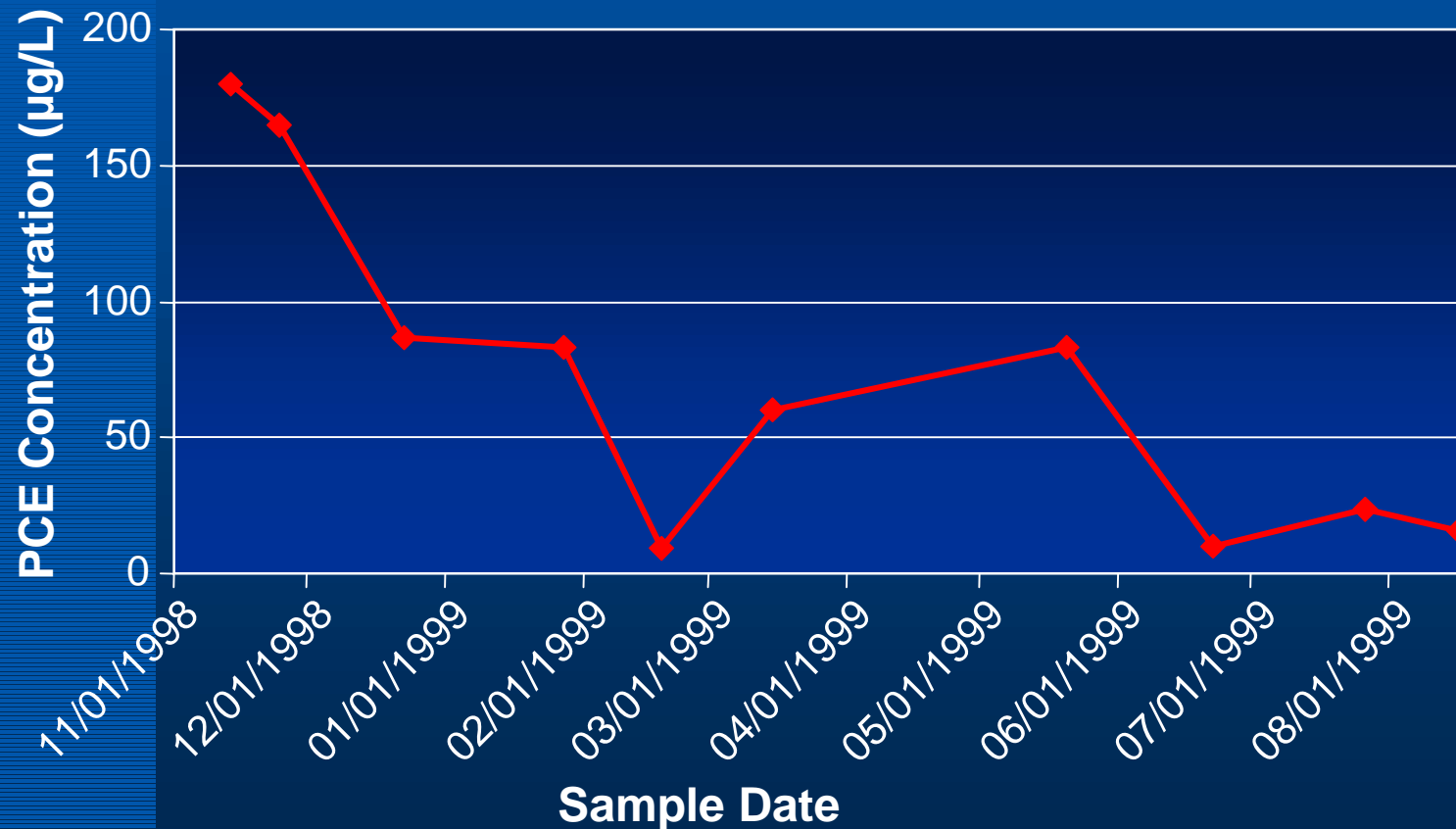
Fenton's Reagent Project: PCE and Total COC Concentrations



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: PCE Concentrations

KBA-11-34



Case History: NSB Kings Bay, GA

Fenton's Reagent Project: Sampling Results, Natural Attenuation

Total VOCs (ppb)

Well	June 1999	July 1999	August 1999
KBA-11-34	10	24	16
KBA-11-32	19	13	12
KBA-11-36	0	17	30
INJ-11	9	8	5

Case History: NSB Kings Bay, GA

Summary

- 99% reduction in total VOCs (source area)
- Regulators withdrew consent order, P&T system turned off
- MNA implemented as final remedy, in accordance with ROD
- Project received Environmental Excellence Award from Georgia Chamber of Commerce
- Life cycle, net present value savings: \$3.3 million

Case History: NAS Pensacola, FL

Fenton's Reagent Project

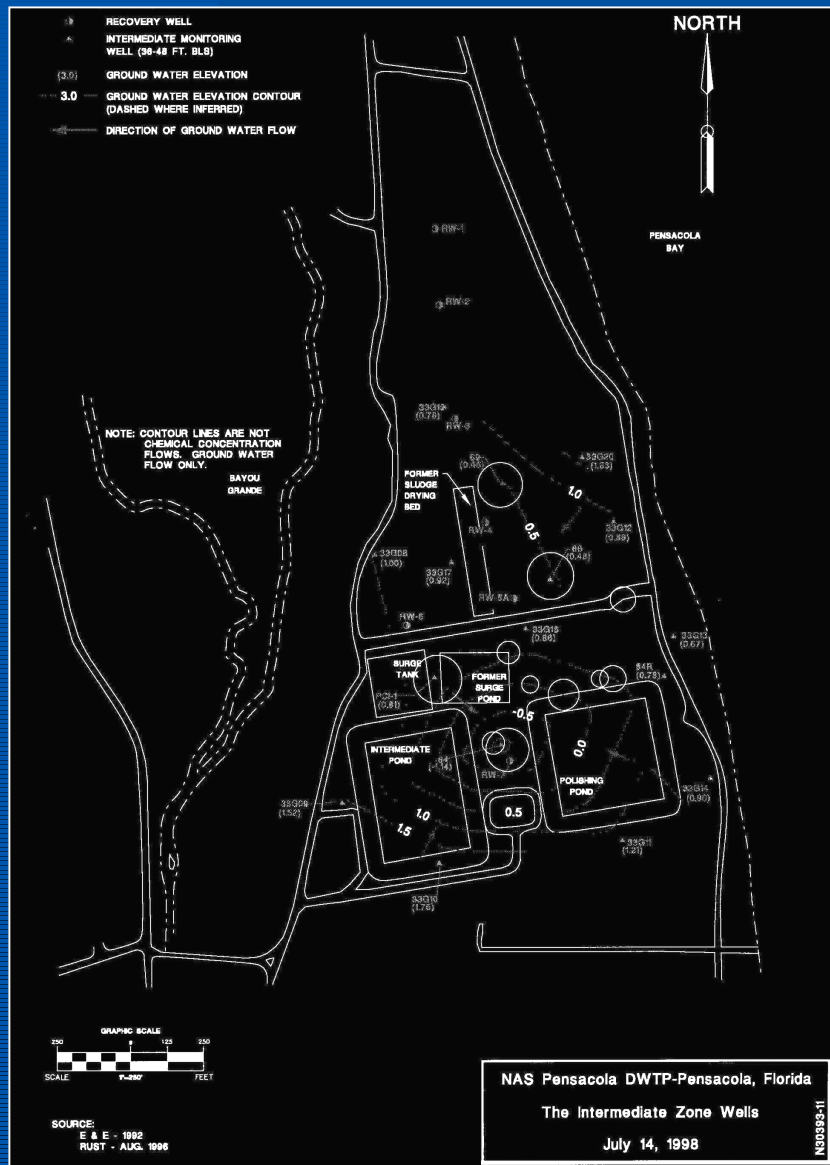
In Situ Chemical Oxidation and Natural Attenuation



- Industrial wastewater treatment plant
- Sandy soils, depth to water ~4 feet
- Contaminants: TCE and degradation products

Case History: NAS Pensacola, FL

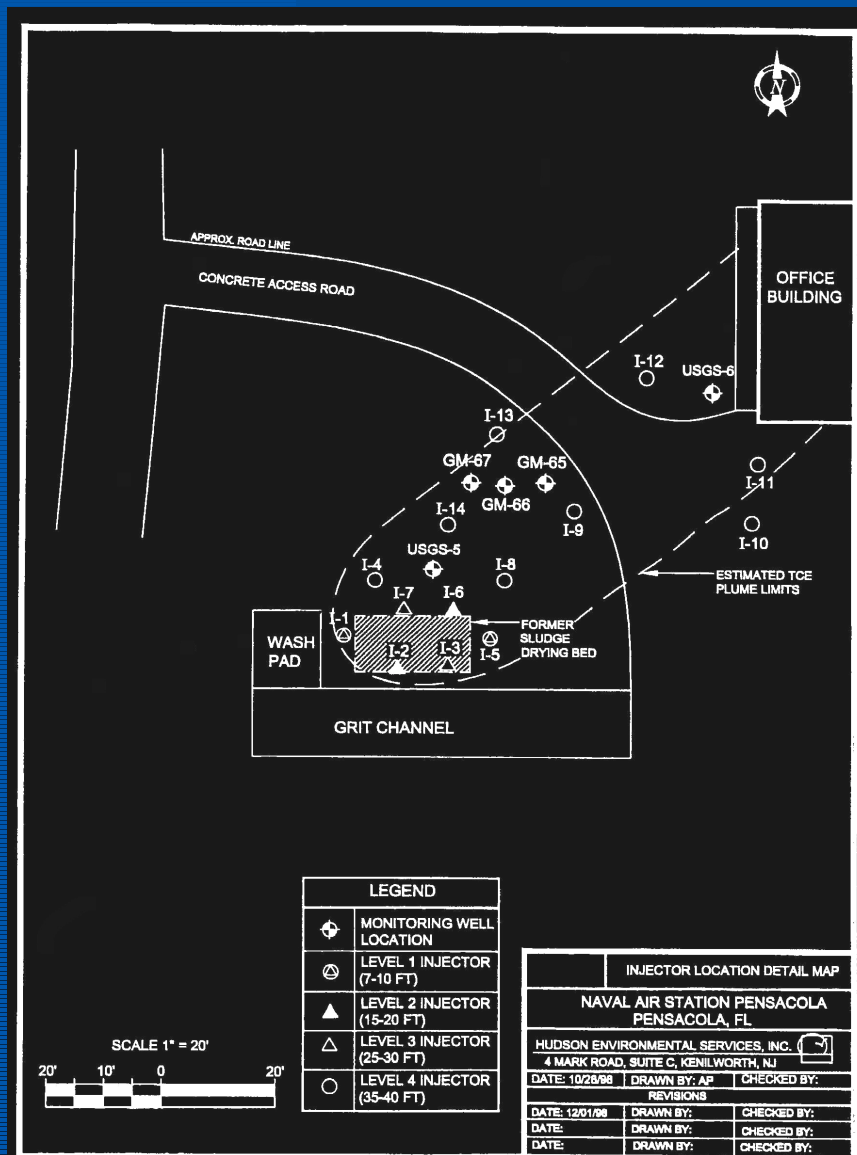
Fenton's Reagent Project: Site Information



- Sludge drying beds, surge ponds
- Soil source areas removed: 1989
- P&T containment: since 1991
- Recovery wells and monitoring wells reduced: 1995
- MNA: since 1996

Case History: NAS Pensacola, FL

Fenton's Reagent Project: Source Area



- 30 ft x 80 ft source area of COCs
- Confining clay layer at about 40 ft bgs
- COCs concentrated at 35- to 40-ft depths
- TCE 3,000 ppb in source area

Case History: NAS Pensacola, FL

Fenton's Reagent Project: Remediation Goals

- Minimize RAO/LTM costs; terminate existing P&T system
- Substantial reduction of source area concentrations
- Ensure that natural attenuation will be an effective final remedy for the remaining dissolved plume
- Protect the downgradient receptor (Pensacola Bay), 500 feet from the source (stable plume)
- Demonstrate the ability to oxidize and treat the TCE source area
- Project conducted under the Navy's Y0817 program, using the Broad Agency Announcement (BAA) contract procedures (Geo-Cleanse International, Inc.)

Case History: NAS Pensacola, FL

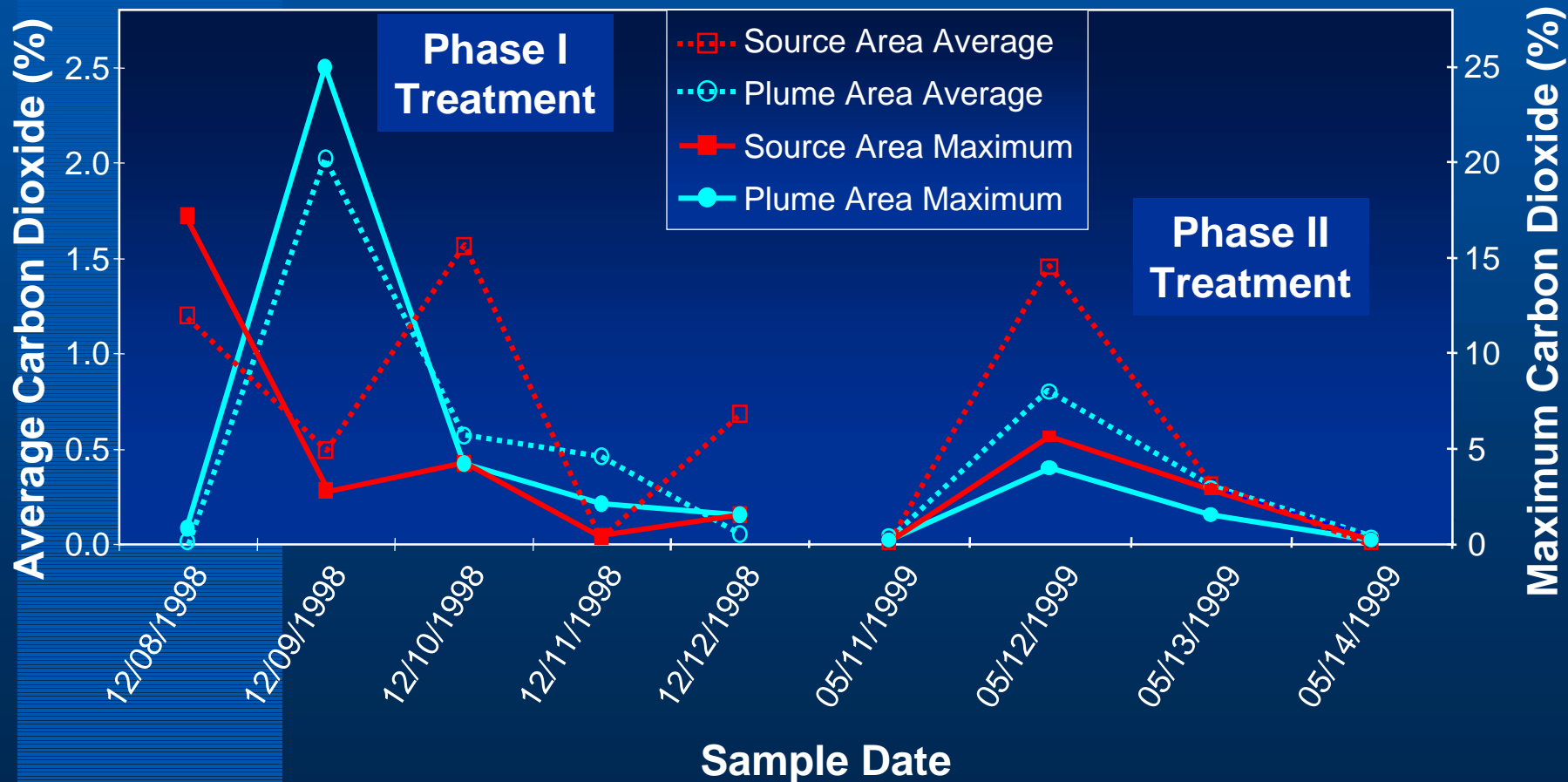
Fenton's Reagent Project: Injection Details



- 15 Injection wells
- 4 levels (7–40 ft)
- Injection duration
 - Phase I: 5 days
 - Phase II: 5 days
- H_2O_2 (50% solution)
 - Phase I: 4,089 gal
 - Phase II: 6,038 gal
 - Total: 10,127 gal
- Similar amounts of FeSO_4 and buffers

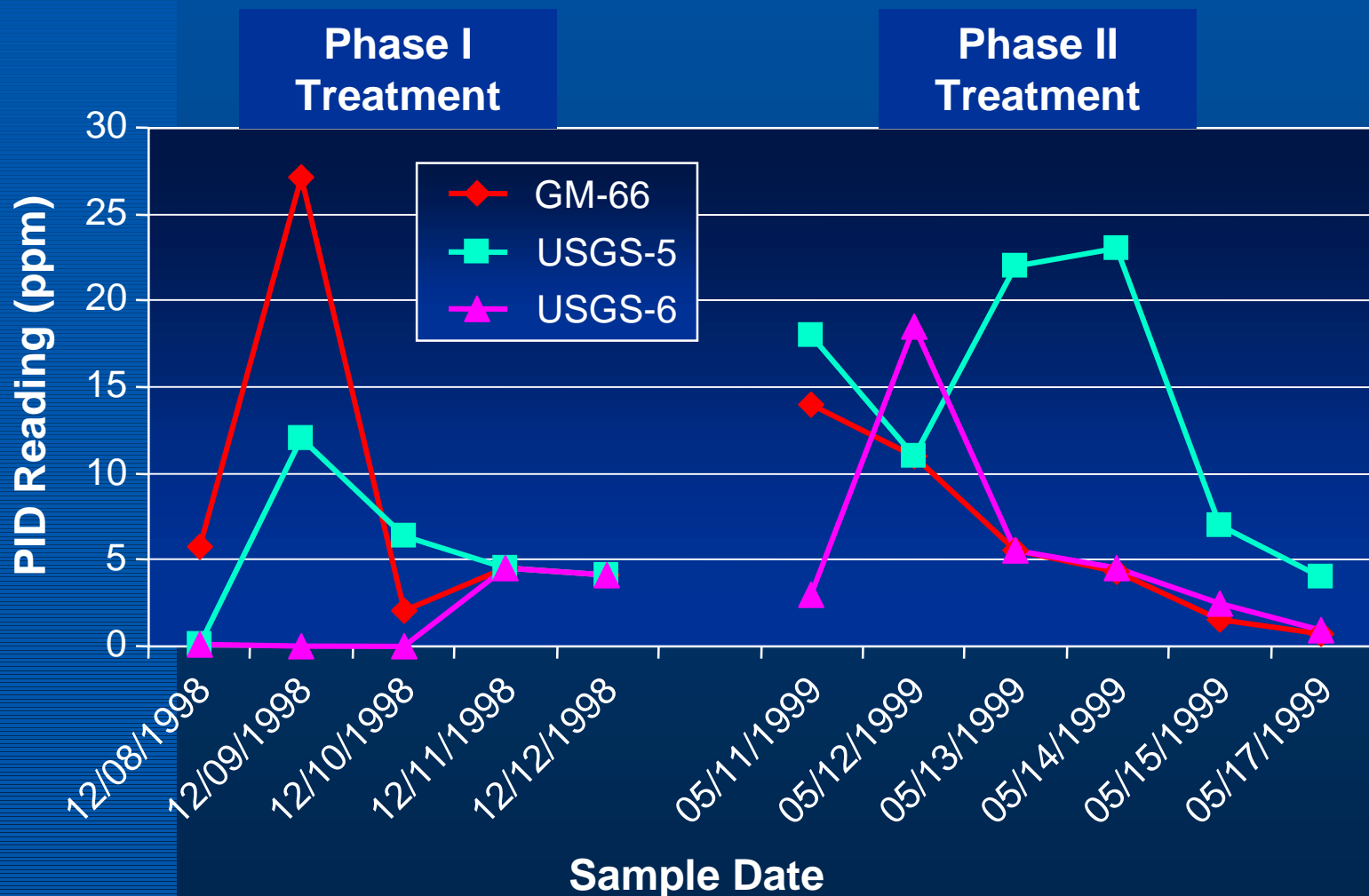
Case History: NAS Pensacola, FL

Fenton's Reagent Project: Carbon Dioxide Off-Gas Results



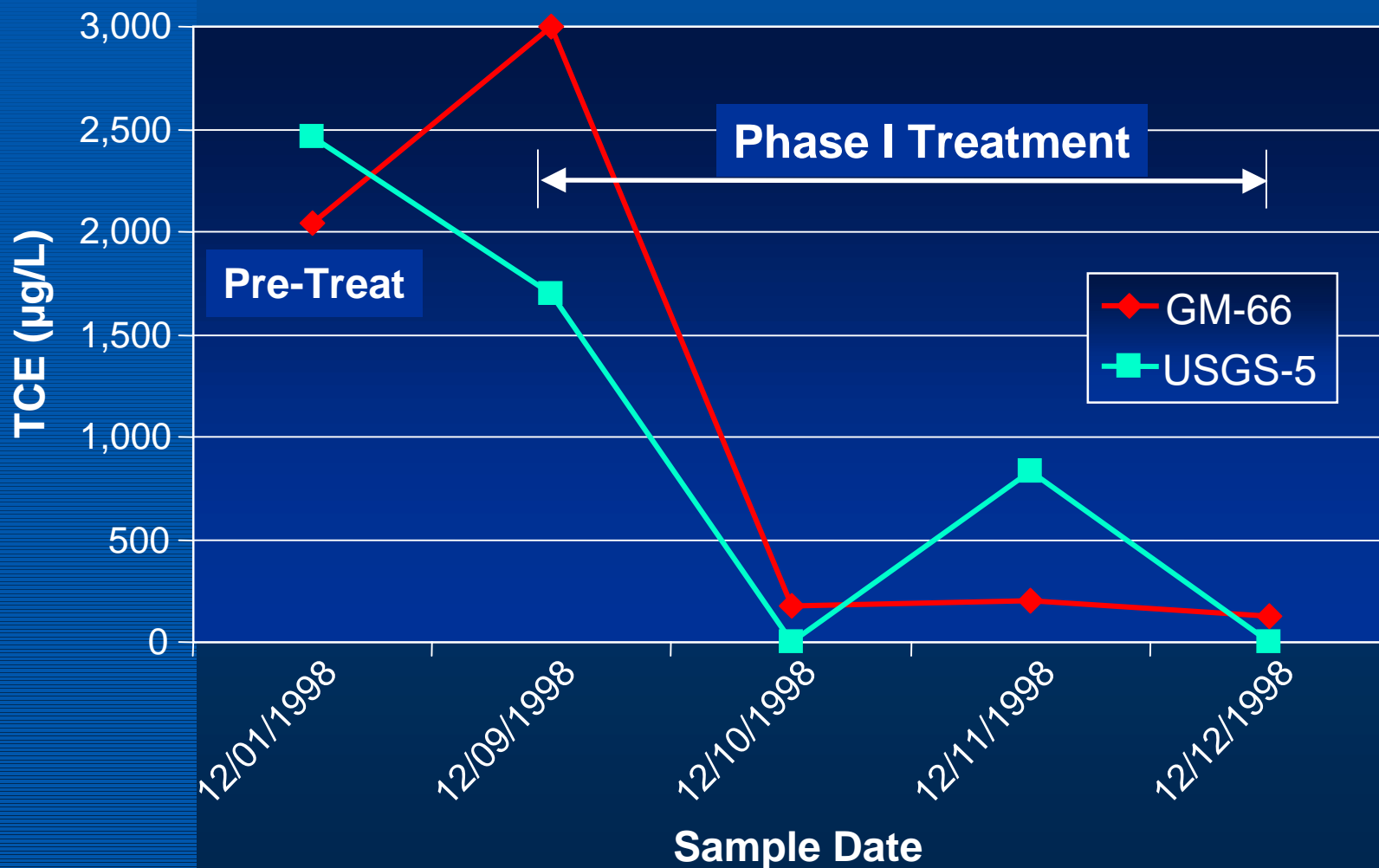
Case History: NAS Pensacola, FL

Fenton's Reagent Project: GW Headspace PID Measurements



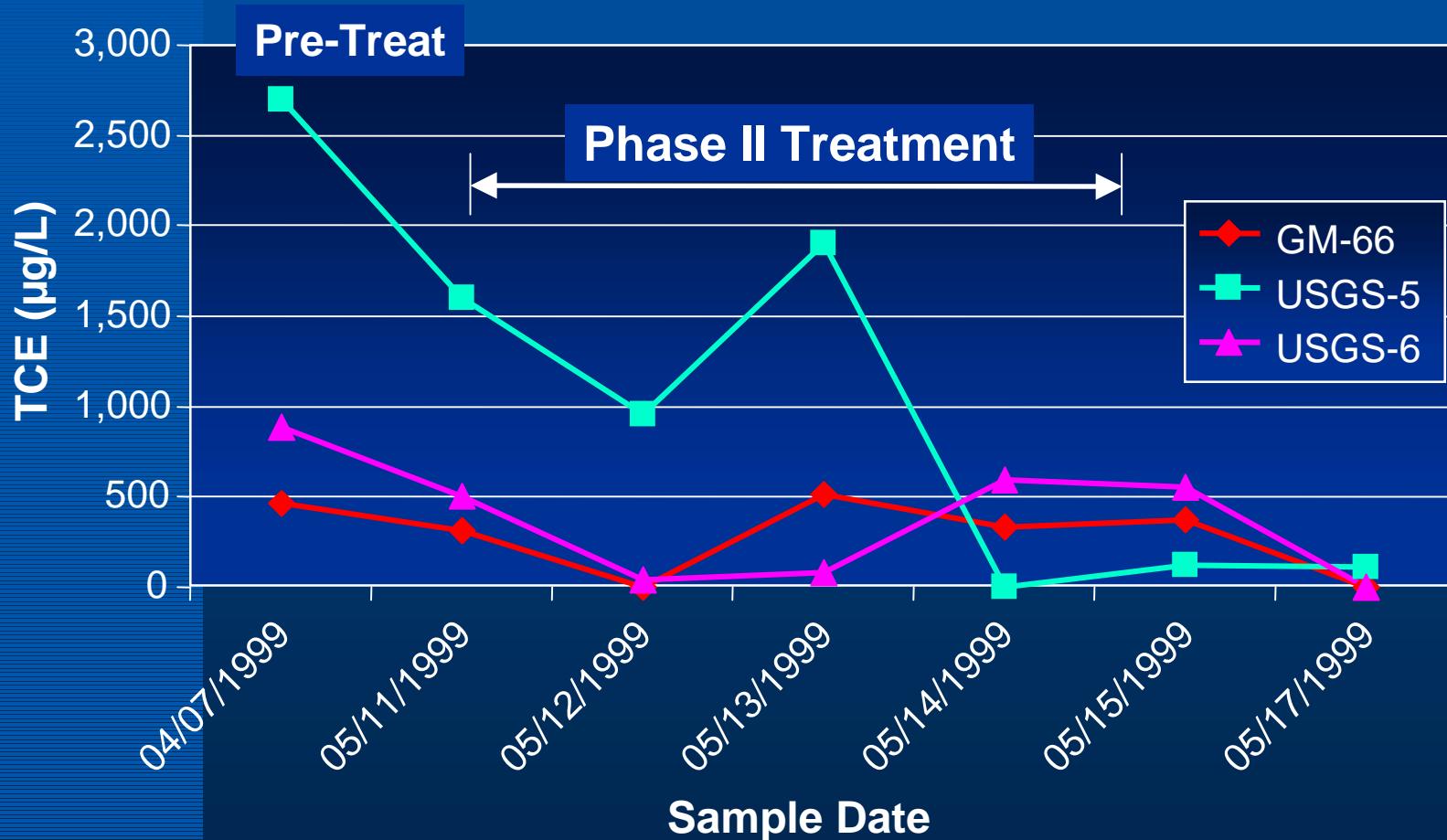
Case History: NAS Pensacola, FL

Fenton's Reagent Project: TCE Results, Phase I



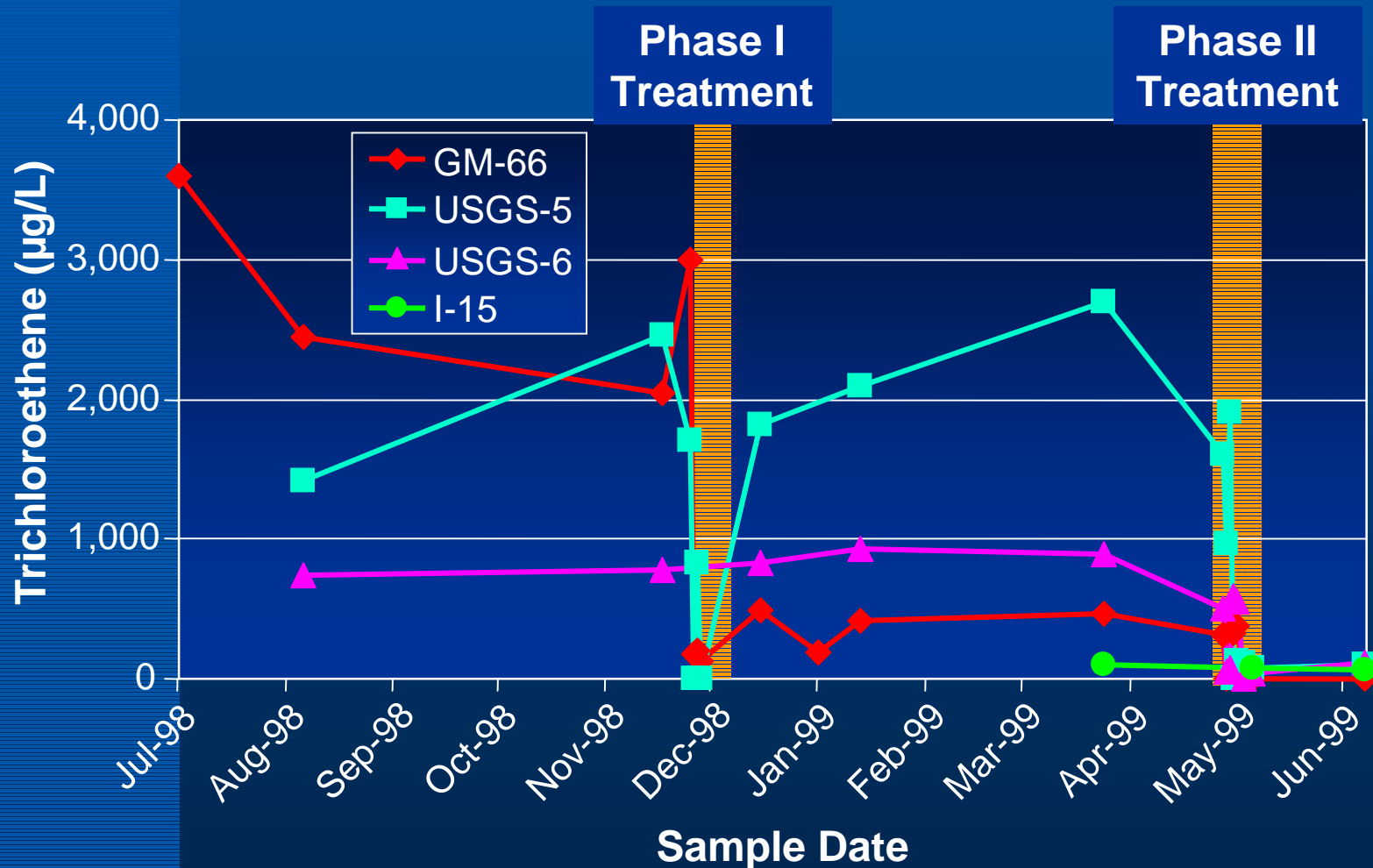
Case History: NAS Pensacola, FL

Fenton's Reagent Project: TCE Results, Phase II



Case History: NAS Pensacola, FL

Fenton's Reagent Project: TCE Results, Phases I and II



Case History: NAS Pensacola, FL

Fenton's Reagent Project: Cost Analysis

Item	Cost
Labor	\$72,000
Per diem	\$8,400
Reagent (H ₂ O ₂)	\$50,000
Installation of injection wells	\$30,000
Injection equipment and transportation	\$20,000
Misc. (10% of all cost)	\$18,500
Sampling and analysis	\$21,000
Total	\$220,000

Case History: NAS Pensacola, FL

Fenton's Reagent Project: Conclusions

- Phase I treatment achieved 87% reduction in GM-66, but not as effective in USGS-5 or USGS-6
- Exceptionally high dissolved Fe(II) levels likely reduced overall effectiveness and radius of influence
- Modified catalyst to enhance and stabilize the reaction, improving distribution and efficiency
- Phase II treatment achieved 96%–100% reduction in source area concentrations
- Enhanced MNA remediation plan

Case History: NAS Pensacola, FL

Fenton's Reagent Project: Summary

- Successfully demonstrated Fenton's Reagent project and validated the technology at this site under specific conditions (sandy aquifer)
- Performance data and end-results met all regulatory expectations. The RCRA CAP permit is being modified to implement MNA as the final remedy.
- Saved \$2 million in life cycle costs from P&T scenario, and accelerated the site closeout by 20 years
- Cost and Performance Report is being prepared and will soon be ready for distribution (NFESC Web site)

Case History: NAS Pensacola, FL

Fenton's Reagent Project: Summary

- Technology is a relatively simple, safe, fast, and cost-effective in situ chemical treatment
- Treatment effectiveness hinges on the chemical injection solution and effective dispersion
- Success is dependent on a number of factors:
 - Contaminant plume characterization
 - Hydrogeologic conditions (highly permeable aquifers)
 - Geochemistry (pH, alkalinity, dissolved iron)

KMnO₄ Injection Case Studies

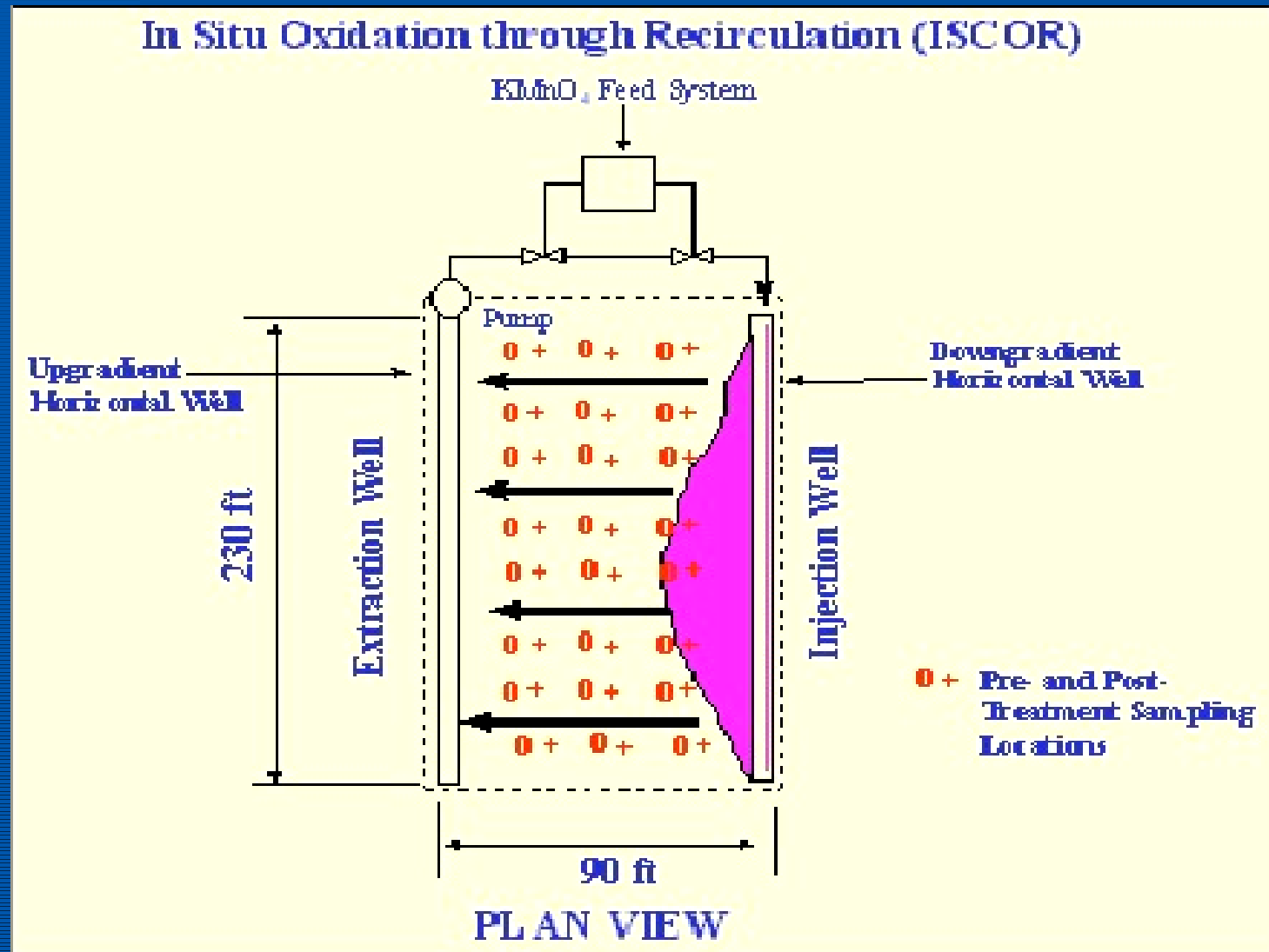
In situ chemical oxidation

- DoD Project
 - Army Cold Regions Research and Engineering Lab (Hanover, NH)
- DOE Projects
 - Kansas City (MO) Plant
 - Portsmouth (OH) Gaseous Diffusion Plant

Army Cold Regions Research and Engineering Laboratory (CRREL) Project

- Groundwater is 130 ft bgs
- TCE DNAPL present 25 ft bgs perched on an intermittent clay lens
- Bio-based remediation was ruled out because of restrictive capillary effects with clay
- KMnO_4 was chosen because of its slow reaction rate; it diffuses slowly into low permeability clays and pH was relatively high
- A 1–1.5 % solution of KMnO_4 will be delivered to the target DNAPL zones through 32 injection points

DOE's ISCOR Process



DOE's ISCOR Accomplishments

- KMnO_4 placement and recirculation using horizontal wells demonstrated at Portsmouth
- Soil mixing using KMnO_4 was used at Kansas City
- Injection using temporary lances was demonstrated at Portsmouth
- KMnO_4 demonstration at Portsmouth using vertical injection, recirculation, and extraction (five-spot pattern)
- Hydraulic fracture and placement of oxidant solids as proponents demonstrated at Portsmouth

KMnO₄ Summary

- Fewer demonstration projects (relatively new)
- KMnO₄ is typically injected in vertical wells and extracted downgradient, then recirculated
- Less aggressive and slower reaction than H₂O₂
- KMnO₄ is a more selective oxidizing agent than Fenton's reagent (simple chlorinated hydrocarbons)
- KMnO₄ not preferred for treating complex ethanes
- Operates in a wider pH and alkalinity range than Fenton's Reagent and under lower permeability conditions

Technology Summary

- In situ chemical oxidation can be a superior and cost-effective remedial option for recalcitrant organics
- Great for source areas; not for total plume management
- Application of technology is not restricted by depth, but may be limited by site geology and geochemistry
- Site conditions may dictate which chemical oxidation treatment methods are appropriate; complete plume delineation and site characterization are important
- Residual oxidizing agents and byproducts are benign
- Chemical oxidation technologies work well with MNA

Tech Transfer Tools

■ Documents

- Geo-Cleanse Reports
- SOUTHDIV Publications
- NFESC Cost and Performance Report
- RPM Newsletter

■ Web sites

- EPA
- DOE
- NFESC (CD-ROM Info)

■ Technical publications

- *Environmental Science and Technology*
- *Ground Water*

References for Additional Information

- Wickramanayake, G., and R. Hincsee, editors. Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, Ohio. May 1998.
- Schnarr, M., C. Truax, G. Farquhar, E. Hood, T. Gonullu, and B. Stickney. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. Journal of Contaminant Hydrology. Vol. 125, No. 5, May 1999.

Points of Contact

- Chuck Reeter (NFESC TAT Lead)
 - Phone: 805-982-4991; e-mail: reetercv@nfesc.navy.mil
- Dr. D.B. Chan (NFESC Tech Spec)
 - Phone: 805-982-4191; e-mail: chandb@nfesc.navy.mil
- Cliff Casey (Navy EFD South Tech Spec)
 - Phone: 843-820-5561; e-mail: caseycc@efdsouth.navfac.navy.mil
- Mike Maughon (Navy EFD South Tech Group Leader)
 - Phone: 843-820-7422; e-mail: maughonmj@efdsouth.navfac.navy.mil
- Anthony Robinson (NSB Kings Bay, GA RPM)
 - Phone: 843-820-7339; e-mail: robinsonab@efdsouth.navfac.navy.mil
- Maxie Keisler (NAS Pensacola, FL RPM)
 - Phone: 843-820-5322; e-mail: keisler@efdsouth.navfac.navy.mil
- Arun Gavaskar (Battelle Project Manager)
 - Phone: 614-424-3403; e-mail: gavaskar@battelle.org